Watershed export events and ecosystem responses in the Mission-Aransas National Estuarine Research Reserve

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Dedication

I dedicate this work to my parents, Tammy McPhee and Edward Mooney, for their endless love and support for everything I do.

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Abstract

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River export has a strong influence on the productivity of coastal waters. During storm events, rivers deliver disproportionate amounts of nutrients and organic matter to estuaries. Anthropogenic changes to the land use/cover (LULC) and water use also have a strong influence on the export of nutrients and organic matter to estuaries. This study specifically addressed the following questions: 1) *How does river water chemistry vary across LULC patterns in the Mission and Aransas river watersheds?* 2) *How do fluxes of water, nutrients, and organic matter in the rivers vary between base flow and storm flow?* 3) *How do variations in nutrient/organic matter concentrations and stable isotope ratios of particulate organic matter (POM) in Copano Bay relate to river inputs?*

Water was collected from the Mission and Aransas rivers and Copano Bay from July, 2007 through November, 2008 and analyzed for concentrations of nitrate,

ammonium, soluble reactive phosphorus (SRP), dissolved organic nitrogen, dissolved organic carbon, particulate organic nitrogen, particulate organic carbon (POC), and the stable C and N isotope ratios of the POM. The first half of the study period captured relatively wet conditions and the second half was relatively dry compared to long term climatology. Riverine export was calculated using the USGS LOADEST model.

The percentage of annual constituent export during storms in 2007 was much greater than in 2008. Concentration-discharge relationships for inorganic nutrients varied between rivers, but concentrations were much higher in the Aransas River due to waste water contributions. Organic matter concentrations increased with flow in both rivers, but POM concentrations in the Aransas River were two fold higher due to large percentages of cultivated crop land. Values of δ^{13}C-POC show a shift from autochthonous to allochthonous organic matter during storm events.

Following storm events in Copano Bay, increases and quick draw down of nitrate and ammonium concentrations coupled with increases and slow draw down of SRP illustrate nitrogen limitation. Organic matter concentrations remained elevated for ~9 months following storm events. The δ^{13}C-POC data show that increased concentrations were specifically related to increased autochthonous production.

Linkages between LULC and nutrient loading to coastal waters are widely recognized, but patterns of nutrient delivery (i.e. timing, duration, and magnitude of watershed export) are often not considered. This study demonstrates the importance of sampling during storm events and defining system-specific discharge-concentration relationships for accurate watershed export estimation. This study also shows that storm inputs can support increased production for extended periods after events. Consideration of nutrient delivery patterns in addition to more traditional studies of LULC effects would support more effective management of coastal ecosystems in the future.

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Introduction

Estuarine ecosystems, defined by the mixing of freshwater and saltwater at land margins, play a critical role in the transport and processing of nutrients and organic matter between watersheds and the coastal ocean. They are also important as commercial and recreational resources. In the Gulf of Mexico, estuarine ecosystems are the home and nursery grounds for numerous shellfish and finfish species that support the regional and national economies. Estuarine-dependent shrimp, menhaden, blue crab, and oyster fisheries are of particular importance in the Gulf of Mexico (NOAA 1990). Human activities are having a profound impact on the ecology and biogeochemistry of estuarine ecosystems worldwide (GESAMP 2001; IPCC 2001a). Land use and land cover (LULC) are linked to exports of water, organic matter, and nutrients from watersheds. As a consequence, changes in LULC such as agricultural development and urbanization lead to significant changes in water, organic matter, and nutrient input to estuarine ecosystems.

Nitrogen loading is of particular importance because N often limits primary production in coastal systems (Vitousek et al. 1997; Cloern 2001) and is the primary cause of increasing coastal eutrophication (GESAMP 2001). Changes in freshwater inputs themselves are important because it is the balance between freshwater input rates and mixing processes that determines the extent and structure of the estuarine salinity gradient. The characteristics of the salinity gradient (i.e. spatial extent and degree of stratification) in turn influence benthic and pelagic community structure and biogeochemical cycling in estuarine ecosystems. The role of watershed-derived organic matter in estuarine ecosystems is less clear. Particulate organic carbon (POC) in rivers is largely recalcitrant (Raymond and Bauer 2001). On the other hand, a significant fraction of watershed-derived dissolved organic carbon (DOC) may be decomposed in coastal waters (Raymond and Bauer 2001), and chromophoric dissolved organic matter (CDOM) in watershed runoff can attenuate light and affect photosynthesis in coastal waters (Blough and Del Vecchio 2002). Impacts related to changes in LULC are expected to intensify in the future with growing human populations in coastal watersheds (GESAMP 2001). In addition, sea level rise and changes in climate patterns associated with global warming are expected to alter estuarine systems dramatically in the future (IPCC 2001a). Exactly how these changes will play out, however, is difficult to predict.

The focus of this study was to examine the relationships between LULC, watershed exports, and estuarine ecosystem properties in the Mission Aransas National Estuarine Research Reserve (Mission-Aransas NERR, Figure 1). Special attention was paid to storm events in defining these relationships. Freshwater exports from watersheds during major storm events deliver pulses of nutrients and organic matter to estuarine systems while at the same time they can alter the salinity structure dramatically. Furthermore, N inputs to coastal waters during storm events may be disproportionately large because N retention and losses to the atmosphere via denitrification during transport through watersheds are far less during storm events (Peterson et al. 2001).

Precipitation in south Texas is highly variable within and between years (Dunton et al. 2001), yet there is limited information on how episodic watershed export events affect estuarine ecosystems in this region. In particular, no studies of watershed export events and estuarine ecosystem responses have been performed in the Copano Bay system. Annual N and P loads to Copano Bay, including contributions from the Mission and Aransas rivers, have been estimated using a GIS based modeling approach (Smith and Dilworth 1999). However, changes in discharge constituent relationships during storm events are not well represented. It is particularly important to improve our understanding of how storm events influence watershed exports and estuarine responses now because the intensity of storms, including hurricanes in the Gulf of Mexico, may be increasing due to global warming (Emanuel 2005). Annual inputs of water, organic matter, and nutrients are, of course, important. However, the timing and magnitude of watershed export events are also important considerations in systems that receive a high percentage of their annual inputs during a few major storms. Thus, *I hypothesize that the timing and magnitude of watershed export events has a primary influence on estuarine ecosystem properties in the Mission-Aransas system.* This contrasts with systems such as the Waquoit Bay NERR which is fed by groundwater at a relatively constant rate (Valiela et al. 1992; McClelland and Valiela 1998).

To address the overarching hypothesis stated above, this study specifically considered three questions: 1) *How does river water chemistry vary with different LULC patterns between the Mission and Aransas watersheds?* 2) *How do exports of water, nutrients, and organic matter from the Mission and Aransas watersheds vary over the year, and what percentages of annual nutrient and organic matter loads to coastal waters are accounted for by storm events versus base flow?* 3) *How do variations in water chemistry and C and N isotope values of particulate organic matter in Copano Bay relate to variations in water, nutrient, and organic matter inputs from the Mission and Aransas rivers?*

Study Area

This study was conducted in South Texas in the Mission and Aransas rivers and Copano Bay from July 2007 through November 2008. The Aransas River flows into the west end of Copano Bay whereas the Mission river flows into Copano Bay more centrally, via Mission Bay (Figure 1). Copano Bay and the lower reaches of the Mission River are a part of the Mission-Aransas National Estuarine Research Reserve (Mission-Aransas NERR; Figure 1). Estuarine conditions in Copano Bay and the lower reaches of the rivers vary widely depending on the frequency and magnitude of regional rain events.

The Mission and Aransas watersheds differ in their size, land use, and land cover characteristics (Figure 2). The Aransas watershed drains 639.7 km^2 with the majority of LULC as cultivated crops (Table 1). In contrast, the Mission watershed drains 1787.1 km^2 with the majority of LULC as shrub land (Table 1). Both watersheds also include multiple permitted waste water treatment plants (WWTP; Figure 2). The Aransas watershed discharges 14.38 million liters per day (mld) from 10 WWTP's, with 8.33 mld from one effluent directly upstream of our sampling site near Skidmore (www.epa.gov/enviro/html/pcs/adhoc.html). The Mission watershed discharges only 1.89 mld discharge from its 3 WWTP's (www.epa.gov/enviro/html/pcs/adhoc.html).

Stream flow in the Mission and Aransas Rivers is generally low with episodic rainfall driving a few large export events each year. During the period of this study the Aransas River discharge ranged from 0.08 to 227.10 $m^3 s^{-1}$, with a mean of 1.51 $m^3 s^{-1}$ and median of 0.18 $m^3 s^{-1}$. The Mission River discharge ranged from 0.01 to 356.79 $m^3 s^{-1}$ with a mean of 4.31 $m^3 s^{-1}$ and median of 0.34 $m^3 s^{-1}$. The lower reaches of these rivers are tidally influenced, the extent of which is a function of the tidal range relative to the elevation change. The average tidal range of Copano Bay is 0.15 m. The U.S.

Geological Survey (USGS) real-time streamflow gage at Refugio, on the Mission River, is 0.31 m above sea level and the gage at Skidmore, on the Aransas River, is 22.06 m above sea level. Forcing from tides coupled with low elevations creates very long mixing rates or residence times in the lower reaches of the rivers. Preliminary modeling on residence times in the tidal reaches of the rivers show large differences between high and low flow conditions (Table 2). As a result, the salinity changes drastically with the hydrologic conditions. During this study, measured salinity ranged from 0.04 to 20.2 psu at the Lower Mission River site and 0.04 to 5.9 psu at the Lower Aransas site.

Copano Bay is a shallow estuary with an average depth of 2 m, surface area of 462.79 km^2, and volume of 0.925 km^3. On average, evaporation exceeds precipitation in this area: Average precipitation is 88.6 cm yr^{-1} and average evaporation 151.3 cm yr^{-1} (Armstrong 1982). Calculated residence times in Copano Bay are as long as 3 years during average conditions (Armstrong 1982). Commercial and recreational fishing and birding are important to the local economy. The major commercial fisheries are shrimp, blue crabs, oysters, spotted sea trout, and black and red drum (Armstrong 1982). Many bird species utilize the Copano Bay area for feeding, such as heron, egret, loon, gull, tern, and duck species (Tunnell et al. 1996). Oyster reefs, wetlands, seagrasses, mangroves, and tidal flats are the habitats that support these valuable species (Figure 1).

Methods

SAMPLE COLLECTION

Samples were collected at upstream sites near Skidmore on the Aransas River and at Refugio on the Mission River, which coincide with USGS real-time streamflow gages (Figure 3). Samples were also collected at two lower sites on the Aransas River, Lower Aransas and Aransas Boat Ramp, and one lower site on the Mission River (Figure 3). In addition, we started sampling Chiltipin Creek, a tributary of the Aransas River, in May 2008 (Figure 3). This site was chosen because it drains a large area, 42.3%, of cultivated crops in the Aransas River Watershed (Figure 2). Two sites in Copano Bay were also sampled, but did not start until 3 weeks after riverine sampling began (Figure 3). Copano East and West are established Mission-Aransas NERR system wide monitoring program (SWMP) sites. The Lower Aransas River site is presented in the results section because it is comparable to the Lower Mission River site. Results from the Aransas Boat Ramp and Chiltipin Creek sites can be found in Appendices B and C.

Surface water samples were collected ~daily during storm events and monthly from July 2007 through November 2008. Temperature, pH, conductivity, salinity, and dissolved oxygen were measured using an YSI multiparameter sonde. Data from Copano East and West were collected during the Mission-Aransas NERR's SWMP field trips by boat. Temperature, pH, salinity, and dissolved oxygen are measured continuously every 15 minutes from an YSI multiparameter sonde at the sampling platforms.

After collection, samples were immediately put on ice. Samples were transported back to the lab and filtered using pre-weighed and pre-combusted Whatman GF/F filters (0.7 μm nominal pore size) within 1-3 hours of collection. Filtered water was stored in high-density polyethylene (HDPE) and polycarbonate bottles (for DOM measurements) in a -20°C freezer until analysis. Filters were dried and post-weighed for particulate organic carbon and nitrogen concentrations (POC, PON) and stable C and N isotope ratios ($\delta^{13}C$, $\delta^{15}N$).

ANALYSIS

Particulate organic matter concentrations and stable isotope ratios were determined using a Carlo Erba 2500 elemental analyzer coupled to a Finnigan MAT Delta+ isotope ratio mass spectrometer. Total dissolved nitrogen (TDN) and dissolved organic carbon (DOC) concentrations were analyzed using a Shimadzu DOC/TN analyzer.

Soluble reactive phosphorus concentrations were measured using a modified version of Murphy and Riley, 1962. Reagents (ammonium molybdate, sulfuric acid, ascorbic acid, and potassium antimony-tartrate solutions) and mixed reagent (ratio of 2:5:2:1, respectively) were prepared according to Strickland and Parson's *Determination of Reactive Phosphorus* (1972). In a 96-well plate, 240 µl of standard or sample, in triplicate, were placed in individual wells. Using a multichannel pipette, 50 µl of mixed reagent was added to each well and read after 5 minutes at 880 nm on a microplate spectrophotometer.

Ammonium concentrations were measured using a modified version of Strickland and Parson's *Determination of Ammonia* (1972). Reagents (sodium nitroprusside, alkaline, and phenol solutions) were prepared according to Strickland and Parsons and Clorox bleach was used for the sodium hypochlorite solution. An oxidizing solution is made, within 5 hours of analysis, with a ratio of 4:1 of the alkaline solution to hypochlorite solution. In a 96-well plate, 220 µl of standard or sample, in triplicate, was placed into individual wells. Using a multichannel pipette, reagents were added to each well in this order: 20 µl of the phenol solution, 20 µl of the sodium nitroprusside solution, and 40 µl of oxidizing solution. The microplate was placed in the dark for 1 hour and then read at 640 nm on a microplate spectrophotometer.

Nitrate+nitrite (referred to hereafter as "nitrate" because the sum is strongly dominated by nitrate) concentrations were measured using a modified version of Jones, 1984. Reagents (ammonium chloride, sulfanilamide, and N-1-napthyl ethylene diamine (NED) solutions) and spongy cadmium were prepared according to Jones, 1984. In 2 ml 96-well plates, 100 µl of the ammonium chloride and 50-100 mg of spongy cadmium were placed in each well. One ml of each standard or sample, in triplicate, were placed in individual wells and incubated horizontally on a shaker at room temperature for 90 minutes. Using a multichannel pipette, 200 ml of each sample were transferred to a new plate; then 20 µl of sulfanilamide and NED were added to each well. Plates were incubated in the dark for 30-90 minutes and read at 543 nm on a microplate spectrophotometer. For all colormetric analyses, concentrations were determined by linear regression of the standard curve. If the absorbance of a sample was outside the standard curves range, it was diluted with nanopure water and re-analyzed.

Dissolved organic nitrogen (DON) concentrations were determined by subtracting dissolved inorganic nitrogen concentrations (sum of nitrate and ammonium concentrations) from total dissolved nitrogen concentrations. When analyzing the DON data by year and site, all data had a strong relationship between DON and DOC except 2008 data from Skidmore (upstream Aransas River). A linear regression of DON versus DOC concentrations from Skidmore in 2007 had an $r^2 = 0.915$ and 2008 data had an $r^2 = 0.013$. A linear regression of DON versus DOC concentrations from the Mission River upstream site at Refugio had a strong correlation in 2007 and 2008, $r^2 = 0.942$ and 0.880 respectively. The lack of correlation between DOC and DON at the Skidmore site during

2008 was attributed to very high concentrations of nitrate: Under these conditions, even small errors (i.e. ± 5%) in nitrate concentration estimate can have a major impact on calculated DON concentrations. Thus, the equation from the DON versus DOC regression from 2007 was used with 2008 DOC data to calculate DON concentrations from 2008. The equation used was

$$DON = 0.0624(DOC) - 11.8966 \quad (1)$$

LoadRunner, software which uses the USGS Load Estimator (LOADEST) program, was used to calculate fluxes of nutrients and organic matter into the estuary (Booth et al. 2007; Runkel et al. 2004). Daily discharge data was downloaded from the USGS real-time water data for Texas website (http://waterdata.usgs.gov/tx/nwis/rt). Discharge data and concentration data (from this study) were used in a multiple regression model to estimate daily fluxes based on flow dependent concentration changes. LOADEST has 11 regression models which the user can pick from or let the model choose based on statistics. For this study the model chosen for all data sets is

$$\ln(\text{export or concentration}) = a_0 + a_1 \ln Q + a_2 \ln Q^2 \quad (2)$$

In this equation lnQ (Q equals discharge) equals ln(Q) minus center of ln(Q), centering the data is applied to eliminate multicollinearity that is associated with multiple regressions (Helsel and Hirsch 2002). Coefficients a_0, a_1, and a_2 are determined by the specific relationships between discharge and constituent concentrations/fluxes measured at the site of interest. Coefficients and statistics are listed in Appendix A. The sign of coefficient a_1 in the concentration statistics tells you whether your concentration increases or decreases with respect to flow and the statistics reveal the significance of the correlation. In this study, LoadRunner input files were daily discharge data from 2007 and 2008 and water chemistry data collected from July 2007 through November 2008. LoadRunner output files were daily chemical export for 2007 and 2008.

The LoadRunner output data were used in analyses for comparisons of storm events and wet versus dry years. Storm events were characterized by having a flow of 10 times greater than the median flow for 2007 & 2008 (Mission River: 3.4 $m^3 s^-$, Aransas River: 1.8 $m^3 s^-$). The range of river discharge from the calibration data was 0.03 to 351.12 $m^3 s^-$ and 0.07 to 239.27 $m^3 s^-$ for the Mission and Aransas rivers respectively. Samples collected in the Aransas River captured the entire range of discharge for 2007 and 2008 and in the Mission River 2007 and 2008 discharge was slightly broader than captured sampling, ranging from 0.01 to 356.79 $m^3 s^-$. For a storm event, the hydrograph had to exceed these conditions and was considered the same storm event until the hydrograph dropped below the criteria. Annual storm event load was the sum of loading from storm event days.

Results

UPSTREAM SITES

River discharge

Water discharge data for the Mission and Aransas rivers during the study period, 2007 and 2008, illustrate a wet and dry year (Figure 4). The 2007 annual flux of water from the Mission River was 2.96×10^8 m^3 y^{-1} and from the Aransas River was 7.97×10^7 m^3 y^{-1}. The 2008 annual flux of water from the Mission River was 6.29×10^6 m^3 y^{-1} and from the Aransas River was 1.03×10^7 m^3 y^{-1}. In general, patterns of discharge (i.e. occurrence of events) were similar between the two rivers.

Inorganic Nutrients

Ranges of nitrate concentrations as well as variability associated with changing runoff differed substantially between the Mission and Aransas rivers. Nitrate concentrations at Refugio (Mission River) ranged from 0.25 to 11 μM whereas nitrate concentrations at Skidmore (Aransas River), ranged from 3 to 627 μM. Nitrate concentrations at Refugio showed an overall positive relationship with runoff (Figure 5a). However, this pattern was not represented well within individual years. During 2007, when runoff ranged between 0.02 mm d^{-1} and 17.25 mm d^{-1}, nitrate concentration was negatively correlated with runoff. During 2008, when runoff ranged between 3.7×10^{-4} mm d^{-1} and 0.18 mm d^{-1}, nitrate concentrations were positively correlated with runoff. At Skidmore, concentrations decreased with increasing runoff during both years (Figure 5b).

Patterns of ammonium concentrations in response to variations in runoff were similar in the Mission and Aransas Rivers, but the ranges of concentrations were different. The bulk of ammonium concentrations at Refugio ranged from 0.25 to 3 μM while ammonium concentrations at Skidmore, ranged from 0.25 to 9 μM. Ammonium concentrations at Refugio and Skidmore increased with increasing runoff until about 0.5 mm d^{-1} (Figure 5c and 5d). When runoff increased above 0.5 mm d^{-1}, ammonium concentrations showed a negative relationship with runoff.

Like nitrate, the ranges of soluble reactive phosphorus (SRP) concentrations and the variability related to changing runoff differed at Refugio and Skidmore. SRP concentrations ranged from 3 to 76 μM at Skidmore and the bulk of the concentrations at Refugio were only from 0.25 to 3 μM. SRP concentrations at Refugio predominantly increased with runoff (Figure 5e). However, at high flow there is variability and it is unclear whether or not there is a dilution effect like the nitrate and ammonium. In contrast, SRP concentrations at Skidmore showed a negative relationship with runoff (Figure 5f).

Organic carbon and nitrogen

Dissolved organic matter concentrations and patterns of variability associated with changes in runoff were similar at Refugio and Skidmore. The range of dissolved organic carbon (DOC) at Refugio was 177 to 1100 μM and at Skidmore was 231 to 888 μM (Figure 6a and 6b). The range of dissolved organic nitrogen (DON) at Refugio was 10 to 51 μM and at Skidmore was 2.5 to 42 μM (Figure 6c and 6d). DOC and DON concentrations increased with increasing runoff at both sites.

Particulate organic carbon (POC) and particulate organic nitrogen (PON) concentrations also increased with increased runoff in both upstream river sites (Figure 6e to 6h). However, particle concentrations reached substantially higher values (~2 fold) in the Aransas River. The bulk of POC concentrations at Refugio ranged from 25 to 254 μM and at Skidmore from 25 to 505 μM (Figure 6e and 6f). Nearly all PON concentrations at Refugio ranged from 3 to 38 μM and at Skidmore from 3 to 60 μM (Figure 6g and 6h).

Stable carbon isotope ratios ($\delta^{13}C$) of POC and patterns associated with runoff were similar between Refugio and Skidmore. The range of $\delta^{13}C$ at Refugio was -33 to -21‰ and at Skidmore was -29 to -18‰, slightly higher than Refugio. A positive relationship between $\delta^{13}C$ and runoff is seen at Refugio and Skidmore during both 2007 and 2008 (Figure 7a and 7b).

Stable nitrogen isotope ratios ($\delta^{15}N$) of PON differed at Refugio and Skidmore, but they showed similar patterns associated with runoff. The range of $\delta^{15}N$ at Skidmore was 1 to 17‰ and at Refugio was only -1 to 7‰, with the exception of one point at 10‰. As runoff increased $\delta^{15}N$ decreased at both Refugio and Skidmore during both years (Figure 7c and 7d).

Riverine export

In general, patterns of nutrient and organic matter export are similar to the discharge patterns shown in Figure 4. However, peaks are enhanced when constituent concentrations are positively correlated with discharge and diminished when constituent concentrations are negatively correlated with discharge. Annualized export results that account for co-variations between concentration and discharge (LoadRunner results) are shown in Tables 3 and 4. Export values calculated using mean concentrations and annual discharge (hereafter referred to as the “manual load calculation”) are also provided in Tables 3 and 4 for comparison. LoadRunner estimates of constituent export from the Mission River are 71 to 102 times greater in 2007 than 2008. When using the manual load calculation, the export estimates are 44 to 89 times greater in 2007 than 2008. For the Aransas River, export values from LoadRunner are 2 to 15 times greater in 2007 than 2008 and export values from manual load calculations are 2 to 10 times greater in 2007 than 2008. The Mission River export from the same years that were calculated using the two methods varied from 4 to 31%. The Aransas River exports from the same year varied from 2 to 48%. Aransas River nitrate and SRP had large differences in export during both years and POC and PON had large differences in 2007 between the 2 methods. On average, for both rivers, the difference between the two methods was greater during 2007, the wet year. Complete LoadRunner statistics are presented in Appendix A.

The contribution of storm events to annual export differed dramatically between the wet (2007) and dry (2008) years (Table 3 and 4). In the Mission River there were 12 storm events in 2007 and only 1 storm event in 2008. In the Aransas River there were 10 storm events in 2007 and 2 storm events in 2008. As a consequence, a much larger proportion of annual export from both rivers occurred during storm events in 2007 as compared to 2008. In the Mission River the percentage of annual export due to storms in 2007 is on average 13 times greater than in 2008 (Table 3). In the Aransas River the percentage of annual export due to storms in 2007 is on average 2 times greater than in 2008 (Table 4).

LOWER RIVER SITES

Inorganic nutrients

Nitrate concentrations and variability associated with storm events were very similar at the lower sites on the Mission and Aransas rivers (Figure 8). Nitrate concentrations ranged from ~0.25 to 15 μM at both sites (with the exception of one higher point in the Aransas) and nitrate concentrations consistently increased during storm events. More specifically, the series of storm events during summer 2007 (focused primarily in July, Figure 4) resulted in elevated nitrate concentrations at both sites (Figure 8a and 8b). In August 2008 the Aransas watershed experienced an additional storm event and there was a consequent increase in nitrate concentrations at the Lower Aransas River site (Figure 8b). In both rivers, nitrate concentrations decreased relatively quickly after individual storm pulses, but repeated events during summer 2007 kept overall values elevated into August in the lower Aransas River and into September in the Lower Mission River. As previously mentioned, the lower river sites are tidally influenced and therefore have a large range of salinities depending on the tides and river discharge. During this study the maximum salinity for the Lower Mission River site was 20.2 psu and for the Lower Aransas River sites was 25.4 psu. During storm events the lower river sites become fresher, thus salinity can be used as a proxy for storm water inputs. A negative correlation between salinity and nitrate concentrations is shown in the salinity plots (Figure 8c and 8d). At the Lower Mission River site nitrate concentrations were elevated in salinities less than 0.4 psu and at the Lower Aransas River site nitrate concentrations were elevated in salinities less than 1.7 psu.

General patterns of ammonium concentrations over time and salinity were similar to those observed for nitrate. However peak ammonium concentrations were lower than peak nitrate concentrations and differences between rivers were more evident. At the Lower Mission River site the range of ammonium concentrations was ~0.25 to 3 µM (Figure 9a and 9c). At the Lower Aransas River site the range of ammonium concentrations was ~0.25 to 7 µM (Figure 9b and 9d). The major storm events throughout July 2007 increased ammonium concentrations at both lower river sites (Figure 9a and 9b). A smaller storm event in late July 2008 is evident in the elevated ammonium concentrations at the Lower Mission River site (Figure 9a). In late August 2008 ammonium concentrations increased at the Lower Aransas River site (Figure 9b) in response to a storm event over the Aransas watershed. After each storm event the elevated ammonium concentrations decreased quickly, but as discussed for nitrate repeated events during summer 2007 kept overall concentrations high for an extended period (Figure 9a and 9b). At the Lower Mission River site ammonium concentrations were elevated in salinities less than 0.4 psu (Figure 9c) and at the Lower Aransas River site ammonium concentrations were elevated in salinities less than 1.7 psu (Figure 9d). Modest increases in ammonium concentrations are also evident at above 10 psu at both locations.

Soluble reactive phosphorus (SRP) concentrations also differed substantially between the lower Mission and Aransas rivers (Figure 10). Concentrations increased in response to storm inputs at both locations, but values ranged from ~0.25 to 4 µM at the Lower Mission River site and ~1 to 15 µM at the Lower Aransas River site. Increases in SRP concentrations at the two sites specifically occurred during/after storm events in July 2007 and August 2008 (Figure 10a and 10b). Again, a strong negative relationship between salinity and SRP concentrations (Figure 10c and 10d) confirms that increases in SRP concentrations were directly linked to storm water inputs. In contrast with the results for nitrate and ammonium, SRP concentrations decreased more gradually after the major storm events in July 2007 (Figure 10a and 10b). This is most evident at the Lower Aransas site where SRP concentrations continued to decline for ~9 months after the July 2007 events. SRP concentrations decreased much faster after the small storm event August 2008.

Organic carbon and nitrogen

Variations in dissolved organic matter concentrations in the lower Mission and Aransas rivers (Figures 11 and 12) were more complex than observed for the inorganic nutrients. The DOC and DON concentration ranges were similar at the two sites: The ranges of DOC and DON concentrations at the Lower Mission River site were 200 to 1090 μM and 15 to 54 μM respectively. The ranges of DOC and DON concentrations at the Lower Aransas River site were 200 to 715 μM and 8 to 44 μM respectively. However, the variability in DOM concentrations was less exclusively coupled with storm inputs than observed for the inorganic nutrients. Concentrations were clearly elevated after the major storm events in July 2007, but they also increased over time during the long drought period of 2008 (Figure 11a, 11b; Figure 12a, 12b). The complexity of the DOM dynamics is further demonstrated by the brief but substantial decreases in DOC (Figure 11b) and DON (Figure 12b) concentrations at the Lower Aransas River site during the first major storm event. At the Lower Mission River site DOC and DON concentrations ranges were 378 to 797 μM and 24 to 46 μM respectively at salinities greater than 2.4 psu (Figure 11c and 12c). Below 2.4 psu, the DOC and DON concentrations initially decrease to minima of 234 μM and 16 μM and then increase to maxima of 1090 μM and 54 μM respectively. This bi-modal pattern was less pronounced but still evident in at the Lower Aransas River site (Figure 11d and 12d).

Particulate organic matter (POM) concentrations at both lower river sites increased during storm events, but relationships with salinity were relatively weak and overall concentrations were higher and more variable in the lower Aransas River (Figures 13 and 14). At the Lower Mission River site, ranges of POC and PON concentrations were 50 to 560 μM and 8 to 76 μM respectively. At the Lower Aransas River site, ranges of POC and PON concentrations were 95 to 666 μM and 14 to 96 μM respectively. POC and PON concentrations specifically increased during July 2007 and August 2008. A general increase in POM concentrations with decreasing salinity in the lower Mission River (Figures 13c and 14c) is consistent with particle contributions from storm water. PON concentrations also increase with decreasing salinity at the Lower Aransas River site (Figure 14d). However, wide scatter in this relationship (and an even weaker relationship for POC versus salinity) indicates that factors other than storm water contributions had a dominant influence on POM concentrations at the Lower Aransas River site.

The $\delta^{13}C$ values of POC spanned a wider range and showed stronger patterns of change over time and salinity in the lower Mission River than in the lower Aransas River (Figure 15). The range of POC $\delta^{13}C$ values at the Lower Mission River site was -34‰ to -21‰. The range of $\delta^{13}C$ at the Lower Aransas River site was -29‰ to -19‰. At the Lower Mission River site, POC $\delta^{13}C$ values decreased between July 2007 and January 2008 and then increase gradually through July 2008 (Figure 15a). Values peaked briefly in July and August 2008 and then decreased again. The highest POC $\delta^{13}C$ values were associated with storm flows (Figure 15a and 15c, low end of the salinity range), whereas the lowest POC $\delta^{13}C$ values occurred around 1 psu. A negative correlation between POC $\delta^{13}C$ values and salinity below 1 psu and a positive correlation between POC $\delta^{13}C$ values and salinity thereafter indicates mixing among at least three carbon sources in the lower Mission River. POC $\delta^{13}C$ values at the Lower Aransas River site also increased during storm events (Figure 15b and 15d, low end of the salinity range), but the effect was less pronounced and there was no evidence of separate mixing relationships across the lower and upper ends of the salinity range.

The $\delta^{15}N$ values of PON showed stronger patterns over time and with salinity in the lower Mission River than the lower Aransas River (Figure 16). The ranges of PON

$\delta^{15}N$ were similar at the Lower Mission River and Lower Aransas River sites, ~-2‰ to 7‰ and ~-2‰ to 8‰ respectively. At the lower Mission and Aransas river sites $\delta^{15}N$ decreased during a major storm event beginning in July 2007 and remained low due to repeated storm events through September (Figure 16a and 16b). Following those events, $\delta^{15}N$ at the Lower Mission River site increased and remained constant until small decreases in July and August 2008. Decreased $\delta^{15}N$ in August 2008 was associated with a small storm event (Figure 16a) and in July 2008 the river runoff did not increase to what we have defined as a "storm event" but there was precipitation on the Mission watershed due to a tropical storm. The lowest PON $\delta^{15}N$ values occurred with the lowest salinities (storm flow) and the highest PON $\delta^{15}N$ values occurred at salinities of about 2 psu (Figure 16c). PON $\delta^{15}N$ was more variable at the Lower Aransas River site and shows decreased values in January and March associated with salinities of 7 and 10 psu (Figure 16b). The overall range of $\delta^{15}N$ decreased and tightened below salinities of 1 psu (1‰ to 5‰, Figure 16d).

COPANO BAY

Salinity

Copano Bay salinity decreased from 12 to 2 psu during the beginning of July 2007 due to a major storm event (Figure 17). Recurring storm events extending into September helped keep the salinity low. After September 2007 salinity gradually increased, but it took until January 2008 to return to 12 psu. Salinity continued to rise as a consequence of persistent dry conditions during 2008, reaching values over 30 psu by the end of the study period.

Inorganic nutrients

Storm events had a large and lasting impact on SRP concentrations in Copano Bay. The overall range of SRP concentrations in Copano Bay was 0.5 to 5.3 μM (Figure 18a and 18b). SRP concentrations were highest when sampling started in late July and decreased for several months thereafter (Figure 18a). It is important to recall that sampling in Copano Bay did not start until ~3 weeks after the first major storm event in July 2007. It is possible that concentrations were higher directly after the first storm event. However, the range of values observed in the Bay in late July (~2 to 5 μM) is within the range of values observed in the lower Mission and Aransas rivers directly after the first major storm (~1 to 10 μM). In August 2008, following a much smaller storm event, there was another increase in SRP concentrations (Figure 18a). The salinity plot shows a clear correlation with increased SRP concentrations and freshwater inflow (Figure 18b).

In contrast with SRP, nitrate and ammonium concentrations were very low in Copano Bay throughout most of the study period. Nitrate concentrations ranged from 0.25 to 3.6 μM (Figure 18c and 18d). Ammonium concentrations ranged from 0.25 to 5.25 μM (Figure 18e and 18f). Concentrations were moderately elevated during late July when sampling began, but dropped to minimum values by early August. As discussed for SRP, concentrations may have been higher after the first major storm event in early July. Recall that nitrate and ammonium concentrations peaked at much higher values in the lower Mission and Aransas rivers after the first major storm event (Figures 8 and 9). In any case, it is clear that nitrate and ammonium concentrations do not remain elevated for extended periods in Copano Bay. There were a few other instances when nitrate and ammonium concentrations in the bay were elevated, but these were not associated with lower salinities (Figure 18d and 18f). In fact, the highest ammonium concentrations measured in Copano Bay occurred toward the upper end of the salinity range.

Organic carbon and nitrogen

In general, patterns of DOM concentrations over time and salinity were similar to those of SRP. Increased DOM concentrations due to storm events remained elevated for many months (Figures 19a and 19c). DOC concentrations during this study period ranged from 251 to 776 μM and DON concentrations ranged from 17 to 34 μM. As previously mentioned, concentrations may have been higher after the first major storm event in early July. In the lower river sites, following the first major storm, DOC and DON peaked at higher concentrations than are observed in the bay (Figures 11 and 12). DON concentrations show peaks at salinities below ~5 psu and at ~25 psu, with the lowest concentrations occurring around 10 psu and above 28 psu, this indicates there is another source (besides storm runoff) of increased DON to the Bay during drought periods (Figure 19d). The same pattern exists for DOC, although the increase around 25 psu is less obvious (Figure 19b).

Similar to the DOM, POM concentrations showed large and lasting effects from storm events in Copano Bay. During this study period POC concentrations ranged from 25 to 390 μM and PON concentrations ranged from 4 to 40 μM. Following the storm events in the summer of 2007 the POC and PON concentrations remained elevated in Copano Bay until early March and then showed a sharp decline (Figure 20a and 20c). Both POC and PON concentrations decreased with salinity. However, concentrations remained relatively high until salinities reached ~15 to 20 psu and decreases strongly thereafter (Figure 20b and 20d).

As observed for POC concentrations, $\delta^{13}C$ of POC in Copano Bay was markedly different between the first and second halves of the study period. The overall range of $\delta^{13}C$ values observed during this study was -29.6‰ to -20.7‰ (Figure 21a and 21b). However, $\delta^{13}C$ values increased rapidly over the month of May. This shift to higher POC $\delta^{13}C$ values was correlated with higher salinities, changing most substantially between 10 and 20 psu. In addition to the major increase in POC $\delta^{13}C$ between the first and second halves of the study period, a decrease in POC $\delta^{13}C$ was evident between the time sampling began (late July 2007) and January 2008. Higher $\delta^{13}C$ values were associated with lower salinities during this early period (Figure 21c), and were consistent with higher $\delta^{13}C$ values for POC in the lower Mission and Aransas rivers direcly after the first major strom event in early July 2007 (Figure 15).

Patterns of PON $\delta^{15}N$ in Copano Bay were less evident over time and salinity than those observed for $\delta^{13}C$ of POC. Overall, $\delta^{15}N$ values ranged from 1.5‰ to 8‰, but most values were above 3‰. The lower values were found during March and April 2008 and were associated with salinities between 10 and 20 psu (Figure 21d). Initial $\delta^{15}N$ values of PON measured in Copano Bay in late July 2007 (Figure 21c) were, on average, higher than those observed in the lower Mission and Aransas rivers directly after the first storm event in early July 2007.

Discussion

OVERVIEW

The Copano Bay system is characterized by low base flows and periodic storm events with associated increased freshwater inflow (Orlando et al. 1993). The full range of inter-annual variability of the region's precipitation patterns (Dunton et al. 2001) is captured during the 2 years of this study. Based on the average discharge for the past 20 years in the Mission and Aransas rivers, 2007 was the 2nd wettest year and 2008 was the 2nd and 4th driest years respectively. Alterations in the physical environment as a consequence of highly variable precipitation are manifest in the wide range of salinities observed in Copano Bay during the study period. Vast differences in export to the estuary between flow regimes fundamentally affect production in the system. Differences in export between high and low flow are not only dependent on changes in river water discharge, but also variations in chemical concentrations with flow. The importance of storm events as contributors to annual watershed export is most clearly exemplified by river discharge data from 2007, when the Mission River had 86 days of storm events which accounted for 92% of the annual water export and the Aransas River had 45 days of storm events which accounted for 88% of the annual water export. Still, in 2008, when storm events only took up 1 day in the Mission River and 6 days in the Aransas River, the percent of annual water export due to storms was 5 and 50% respectively. Following storm events, Copano Bay is supported by these inputs for relatively long periods of time.

The Mission and Aransas watersheds experience 76 to 97 cm of precipitation per year (based on 30 years of data; University of Utah 2009). Annual precipitation for the region is comparable to cities such as Dallas, TX, Des Moines, IA, Milwaukee, WI, Rochester, NY, and Seattle, WA (University of Utah 2009). Although the annual amount of precipitation is similar, the patterns are very different (Figure 22). The precipitation patterns in Seattle and other cities in the Pacific Northwest are high in the fall, winter, and spring, and low in the summer months. In contrast, those cities in the mid-west have dry winters and the highest precipitation in the summer. South Texas precipitation is also lower during the winter months than other times of the year, but the seasonality is less pronounced. Furthermore, much of the precipitation falling in the South Texas region between May and September is delivered during tropical storms that vary widely with respect to timing, frequency, and intensity from year to year. Emphasis on storm events becomes critically important when considering coastal systems that receive most of their watershed inputs during a few large runoff events each year. However, even in systems receiving more consistent runoff, storm events are under-represented in routine sampling programs and may be more influential than is generally realized.

EXPORT FROM THE MISSION AND ARANSAS RIVER WATERSHEDS

On average, annual precipitation in Texas is greater to the east (Figure 23). This is not only evident across the state but also in comparing precipitation patterns between the Mission and Aransas watersheds. Thus, we might expect to see greater discharge from the Mission River watershed as compared to the Aransas River watershed. Water discharge from the Mission River is also expected to be higher because the catchment area above the sampling site at Refugio is 6.5 times larger than the catchment area above the sampling site at Skidmore. However, in 2008 the annual discharge in the Aransas River surpassed that of the Mission River. As discussed earlier, the Aransas watershed has ~8 times the amount of wastewater effluent in the watershed than the Mission and over half is located directly upstream of Skidmore (Figure 2). These additional sources of water are the main contributor to higher flows in the Aransas River during droughts. During median flow the contribution to river discharge from the WWTP discharge is 0.5% and 84% in the Mission and Aransas rivers respectively (river discharge data from time period of WWTP discharge monitoring).

Annual export, as previously mentioned, is dominated by periodic storm events. On average, the Mission and Aransas watersheds experience about 9 storm events per year. In 2007 the Mission River had 12 storm events and the Aransas River had 10 storm events. In contrast, during 2008 the Mission River watershed had 1 event and the Aransas River watershed had 2 events. Although the number of events in 2007 was just above average, the magnitude of those events was large in comparison. In contrast, the number of storms and export from 2008 in both rivers was far below average. Because of this variability, it is important to place emphasis on the timing of nutrient and organic matter export, as opposed to only considering annualized values, when looking at the downstream ecosystem response.

Comparison between export calculations from LoadRunner and the "manual load calculation" (multiplying average annual concentration by annual river discharge) resulted in large differences in export estimates. It has been known that variations in discharge on a daily basis versus annual flow are more important for controlling export (Howarth et al. 1991), yet export calculations are constantly over simplified. Export from the Mission River in 2007 was higher from LoadRunner than from the manual load calculation whereas the opposite was true for 2008 (with the exception of nitrate). These differences are specifically attributed to variations in concentration with discharge that are accounted for in the LoadRunner estimate but not in the manual load calculations. When constituent concentrations are positively correlated with discharge, the manual load calculation underestimates export during storm events and overestimates export during low flow. The opposite is true for constituents that are negatively correlated with discharge. While these effects are clearly evident in the Mission River, they are even more pronounced in the Aransas River, where constituent concentrations vary more widely with discharge. In the case of nitrate and SRP, which dilute with flow, the export is overestimated by 26 to 40% with the manual load calculation. PON and POC in the Aransas River are underestimated by 48 and 47% during 2007 because the manual load calculation doesn't consider increases in concentration with the storm events. In 2008 the POC and PON export in the Aransas River was only 2 to 3% different between the two methods because there were only 2 storms.

The different behavior of inorganic nutrients in response to flow at Refugio and Skidmore is attributed to anthropogenic inputs. More specifically, the high concentrations of inorganic nutrients found at Skidmore are consistent with wastewater effluent contributions from the outfall located directly upstream of the sampling site (Figure 2). During low flow nitrate concentrations were as high as 627 μM at Skidmore and only 11 μM at Refugio (Figure 5). When flow increases, the high concentrations of nitrate and SRP are diluted out at the Skidmore site. Long periods of little to no rain cause nutrients to accumulate in the soil as well. These nutrients are released into the river during rain events with subsequent increases in concentrations at Refugio (Meyer et al. 1988), but in Skidmore the WWTP signal is too high to see these smaller terrestrial inputs.

High $\delta^{15}N$ of PON in the Aransas River near Skidmore also suggest anthropogenic inputs of nitrogen into the system. The watershed upstream of the Skidmore sampling site drains 22% cultivated cropland which could lead to increased nitrogen loading, but the high PON $\delta^{15}N$, 17‰, are more indicative of wastewater inputs. Wastewater-derived nitrate $\delta^{15}N$ values are typically in the range of 10-20‰, whereas artificial fertilizer $\delta^{15}N$ values are typically in the range of -4 to 4‰ (Heaton 1986). Primary producers growing in the river under low flow conditions (including phytoplankton that bloom in slow moving "pools" along the river course) have ample time to take up nutrients from the sewage outfall. During high flow, however, this high PON $\delta^{15}N$ is diluted by allochthonous PON inputs with lower $\delta^{15}N$ values from the surrounding landscape (Figure 7). Inorganic nitrogen in rain typically has $\delta^{15}N$ values in the range of -12 to 2‰ (Heaton 1986). Cycling of this nitrogen within the watershed, including uptake by primary producers, microbial remineralization, and denitrification, leads to a relative ^{15}N enrichment of the soil organic nitrogen pool. However, values for natural soil organic matter typically range from 3 to 7‰ (Heaton 1986). A decrease in PON $\delta^{15}N$ to values between approximately 0 and 6‰ during high runoff conditions in the Aransas River is consistent with increasing soil organic matter contributions.

The Mission River watershed upstream of Refugio has lower nutrients and minimal point sources (Figure 2). The LULC of Refugio's drainage area is mainly grass, forest, and shrub land which are sinks for nutrients (Peterjohn and Correll 1984). As mentioned earlier, the increases of inorganic nutrients during high flow could be from accumulated nutrients that are washed out (Meyer et al. 1988). The bulk of PON $\delta^{15}N$ values from Refugio are below 6‰, which is characteristic of natural soil organic matter or phytoplankton growing on a natural inorganic nitrogen source (Peterson and Fry 1987; Heaton 1986). The decrease in $\delta^{15}N$ during storm events does indicate a shift in PON source. This could be a shift from autochthonous to allochthonous PON as described for the Aransas River. However, without a major wastewater source leading to extraordinary enrichment under low flow conditions, the effect is less pronounced in the Mission River.

Differing LULC in these watersheds also can explain the larger POM concentrations (~2 fold) in the Aransas River site during storm events. Skidmore's drainage area contains 22% cultivated crops whereas Refugio's drainage area contains only 2% cultivated crops. Agricultural land is more vulnerable to erosion than unaltered habitats (Walling 1999), such as forest and shrub land, which make up 56% of Refugio's drainage area. A study in the Rhode River watershed found agricultural land to have the highest export of total organic carbon (Correll et al. 2001). In the Hudson River watershed a generalized watershed loading model found that agricultural and urban land disproportionately exported the majority of the total organic carbon (Howarth et al. 1991). In addition, as land is cultivated from forest the soil properties change and loss of organic matter occurs (Lugo et al. 1986).

Increased $\delta^{13}C$ of particles with runoff (Figure 7) confirms a shift from autochthonous to allochthonous sources. For both rivers, the POC $\delta^{13}C$ values measured during low flow are comparable to the $\delta^{13}C$ of autochthonous producers that have been measured in many freshwater systems (Peterson and Fry 1987). The relatively low $\delta^{13}C$ values result from significant contributions of respired CO_2 during carbon fixation when mixing of atmospheric CO_2 across the air-water interface is limited. During high flow, POM $\delta^{13}C$ increases due to terrestrial runoff. The allochthonous inputs of POC have a higher $\delta^{13}C$ value because they are derived from a mix of C_3 (-28‰) and C_4 (-13‰) plants (Peterson and Fry 1987). Texas has a hot and dry climate; consequently 68% of grasses are C_4 grasses (Teeri and Stowe 1976) and 30% of the Mission-Aransas watershed is grasslands. In addition, the major crops in this region include C_4 plants sorghum and corn. As previously mentioned, POM concentrations are higher in the Aransas due to cultivation. This may also explain the higher $\delta^{13}C$ values of POC found in the Aransas River as compared the Mission River.

COPANO BAY RESPONSE

In this study, emphasis has been placed on the variability of precipitation in this region within and between years. The effects are not only seen in the variations in the nutrients and organic matter but the freshwater input itself which dramatically changed Copano Bay's environment. Changes in the salinity regime are known to change rates of productivity and composition of organisms in estuaries (Montagna and Kalke 1992; Russell et al. 2006). Thus, as nutrient dynamics are discussed below, it is important to keep in mind that the community of organisms (both microbial and metazoan) driving nutrient cycling within the system must have changed as well. In particular, the shift from an estuarine to essentially freshwater system during/after the major storms in July 2007 must have greatly impacted the existing benthic community. The benthic community was not examined in this study, however Montagna and Kalke (1992) found in the Guadalupe and Nueces estuaries (directly north and south of Copano Bay) that benthic macrofauna productivity and biomass was higher with increased freshwater inputs and meiofauna density decreased with freshwater inputs. At the same time, sustained low salinity (~2 psu) in Copano Bay for more than a month during July/August 2007 supported the development of temporary planktonic community suited to the freshwater conditions. As the salinity gradually increased over the following months, the community of organisms was obliged to change with it.

Relatively low dissolved inorganic nitrogen concentrations and high SRP concentrations in Copano Bay over an extended period following the major storm events of July 2007 (Figure 18) suggest that nitrogen is the limiting nutrient in this system. Nonetheless, the non-linear behavior of SRP with salinity (Figure 18b) suggest that SRP was drawn down substantially (not simply diluted) between late July and the end of August. Dissolved inorganic nitrogen export from the Mission and Aransas rivers during the storm events of July was sufficient to support the initial draw down of SRP. While uptake of dissolved inorganic nutrients was most evident shortly after the storm events, organic matter dynamics (discussed below) suggest that the inorganic nutrients had an extended effect on the system through recycling.

Increases in DOM concentrations in Copano Bay occurred at two different salinity regimes, indicating there were two sources of DOM. The peak concentrations of allochthonous DOM (low salinities) and autochthonous production during dry periods (high salinities) are roughly equal. The C/N ratio of dissolved organic matter is higher following storm events (Figure 24b). Higher C/N ratios indicate recalcitrant organic matter and lower ratios indicate more labile organic matter. In general, terrestrial derived organic matter have C/N ratios of greater than 15 and higher ratios for degraded terrestrial organic matter (30 to 50; Kendall et al. 2001). Typically, C/N ratios of phytoplankton are 5 to 8 (Kendall et al. 2001). In Copano Bay, the C/N ratios are consistently 10 to 15 and then increase during lower salinities (Figure 24b).

In contrast with the DOM, the POM in Copano Bay is primarily of autochthonous origin. Ratios of carbon to nitrogen are constant across salinities (~ 5 to 8) indicating fresh phytoplankton growth (Figure 24a; Kendall et al 2001). However, the riverine POM inputs C/N ratios are also largely within the same range, therefore the C/N ratios do not confirm the origin of the OM. The POC $\delta^{13}C$ data provide more information (Figure 21): The shift in $\delta^{13}C$ values between the first and second halves of the study period is largely consistent with expected changes in DIC- $\delta^{13}C$ across salinity (Fogel et al. 1992). Values during/after the summer 2007 storm events show some evidence C_4 + C_3 plant contributions, but the signal drops off quickly. The elevated concentrations of POM that occurred for many months following the major storm events in the summer 2007 (Figure 20) are consistent with increased production in response to increased river export. Inputs from storm events sustained higher production through a range of salinities (~0 to 15 psu) for ~9 months in Copano Bay.

The PON stable isotope data from Copano Bay do not shed additional light on the relative importance of autochthonous versus allochthonous sources. However, it is noteworthy that the high $\delta^{15}N$ ratios observed in the upper Aransas River did not have a measurable effect on $\delta^{15}N$ values of PON in the bay. It is likely that the signal at Skidmore is simply overwhelmed by contributions from lower $\delta^{15}N$ sources during high flow. Furthermore, the drainage area for the Skidmore site is only ~13% of the entire Mission-Aransas watershed.

In addition to changing productivity in the water column, increases in DOM and POM due to nutrient loading and/or resuspension of sediments can also cause attenuation of light in estuaries with implications for seagrass production (Duarte 1995). In South Texas, seagrasses are an important habitat and can be sensitive to decreased light (Dunton 1996). A long term brown tide bloom in the Laguna Madre lowered light penetration by 50% and thus lowered seagrass productivity (Dunton 1994). Seagrass beds have also been affected by increased nutrient loading through algal blooms, which include increases in epiphyte cover that results in severe light limitation (Silberstein et al. 1986; Tomasko and Lapointe 1991). Furthermore, high nutrient concentrations are often associated with blooms of drift macroalgae that can out-compete seagrasses at low light levels (Kopecky and Dunton 2006). Unfortunately, the relationship between nutrient concentrations and seagrass response often does not consider nutrient loading (Kopecky and Dunton 2006). As shown in this study, nitrogen is assimilated rapidly within the bay and without knowledge of riverine inputs it would be difficult to know if loading occurred. Therefore, future studies on seagrass systems should consider calculating watershed exports of nutrients and organic matter into their ecosystem.

LOWER RIVER SITES

Located near the mouths of the rivers, the lower sites on the Mission and Aransas rivers are unique because during high flow they are part of a continuum with the river, but during low flow they are more tightly coupled with the bay. Depending on the flow regime, the fresh water residence time in the lower Mission River ranges from <1 day to 5-6 months and in the lower Aransas river ranges from 5 days to 9-11 months. The following discussion emphasizes similarities and differences between patterns observed in Copano Bay and those observed at the lower river sites. Some differences may be attributed to the fact that sampling at the lower river sites began directly after the first storm event whereas sampling in the bay started later. Differences in scale are also an important consideration. The sampling points near the mouths of the rivers represent a very limited geographical extent, whereas the data from the bay (Copano East and Copano West combined) represent a much larger area. Effects of advection become increasingly important at smaller scales.

Overall patterns observed for inorganic nutrients and DOM were similar between Copano Bay and the lower river sites. However, sampling directly after the first storm in July 2007 captured sharp initial peaks that were not observed in the bay. Also, bi-modal patterns in DOM concentrations resulting from different sources of DOM during high and low flow were more pronounced at the lower river sites. Although the Aransas River at Skidmore had much higher concentrations of inorganic nutrients than the Mission River at Refugio, the concentrations seen in the Lower Aransas River site are only modestly higher than in the Lower Mission River. Uptake by phytoplankton may explain why we did not see much higher inorganic nutrients in the lower Aransas River. This explanation is supported by the higher POM concentrations (during low flow in particular) observed at the Lower Aransas River site.

While differences between Copano Bay and the lower river sites were relatively minor with respect to inorganic nutrients and DOM, differences in POM between Copano Bay and the lower river sites were more remarkable. At all sites there was an increase in POM concentrations associated with the storm events, however the isotope data indicate that the organic matter was of different origins. As previously discussed, Copano Bay's increased POM concentrations were dominated by autochthonous production. In contrast, increases in POM at the lower river sites following the storm events in summer 2007 had $\delta^{13}C$ values indicative of major allochthonous contributions. These were gradually replaced by $\delta^{13}C$ values indicative of fresh/oligohaline water production over the remainder of 2007. During 2008, the $\delta^{13}C$ values shifted to reflect autochthonous production under increasingly salty conditions. PON $\delta^{15}N$ also differed substantially between Copano Bay and the lower river sites: Unlike Copano Bay, PON $\delta^{15}N$ at the lower river sites showed a clear relationship with salinity and storm events. Like the upstream sites, this demonstrates a shift to soil organic matter contributions during storm events.

The magnitude of a storm and prior conditions in the watershed must be considered to fully understand the dynamics of each element. In August 2008 a relatively small storm occurred (with precipitation primarily falling on the Aransas watershed), but there was a very large response at the lower Aransas River site. The period prior to this storm event was extremely dry (Figure 4) and some studies have shown that after a drought nitrate peaks during the first major storm and has smaller increases in subsequent storm events (Biron et al. 1999). The major storm event in July 2007 was preceded by a relatively wet year, whereas 2008 was very dry and a relatively small storm showed large increases in nutrients and organic matter. These did not translate into major increases in Copano Bay because the overall flux to the bay was relatively small after the 2008 storm event.

BROADER CONTEXT

Comparison of water, nutrient, and organic matter loading during wet and dry years demonstrated the inter-annual variability this ecosystem experiences and leads to questions of how the system is supported during dry periods (Dunton et al. 2001; Orlando et al. 1993). During storm events, the bay experiences large fluxes of nutrients and organic matter. During dry periods the export from upstream is slowly being mixed into the lower reaches of the rivers and into the bay. Without a significant supply of new nutrients, the bay must depend on recycling of organic matter and nutrients to support productivity. In the Nueces Estuary, south of Copano Bay, microbial processes have been shown to be an important source of nutrients or regeneration of nutrients to the estuary during droughts (Gardner et al. 2006). Nitrogen cycling, during low flow periods, was comparable to eutrophic systems and was supported by high rates of nitrogen fixation. When the estuary was fresher they found more denitrification, dissimilatory nitrate reduction to ammonium (DNRA), and remineralization. A similar study completed in Copano Bay may find some similar results on how this ecosystem supports itself when there are no storm events. In particular, it would be interesting to compare the relative importance of N-fixation versus recycling of land-derived nutrients in Copano Bay over extended dry periods. How long can nutrients delivered during storm events support the system through recycling? The elevated organic matter concentrations (PON in particular) in Copano Bay following the major storms of July 2007 and lasting through March 2008 suggest that recycling of land-derived nutrients remains important for at least a year. However, even as overall productivity drops off, the land-derived nutrients delivered to the bay during storm events may remain the dominant source through recycling.

Wind mixing almost certainly plays an important role in the recycling process. Wind and waves in Copano Bay cause resuspension of particles and sediment throughout the year. A study in Mono Lake, California found that high winds generated internal waves and boundary mixing that resulted in nutrient fluxes out of the sediment and primary production (MacIntyre et al. 1999). In Copano Bay turbulence generated from wind causes resuspension of particles and vertical advection of ammonium out of the sediment could potentially support production during drought conditions. Again, this ammonium could be recycled from watershed inputs or alternative sources. Atmospheric inputs and nitrogen fixation has been found to be an important source of nitrogen to Nueces Bay during droughts (Brock 2001). In addition, Brock (2001) found tidal entrainment from neighboring bays and the Gulf of Mexico to be a source of nitrogen during low flow conditions.

Nutrient concentrations and patterns associated with river discharge vary spatially and temporally. Nutrient supply to rivers is dependent on many factors including geology, hydrology, soil characteristics, LULC, vegetation, and atmospheric inputs. Variations in rivers are further complicated by geographical factors such as temperature (seasons) and precipitation patterns. Meyer et al. (1988) reviewed the relationship between discharge and constituent concentration and found varying results between rivers. Like this study, many others have found adjacent watersheds with different LULC to have different patterns of nutrients and organic matter associated with flow. They found that in all but one river (the Rhode River, MD increased) ammonium did not change with discharge. Although we found patterns with ammonium and discharge, they were not very strong. This is perhaps because ammonium is assimilated quickly and is regenerated from remineralization of organic matter. Nitrate and SRP behavior varies in the literature and also varied between the two rivers in this study. Meyer et al. (1988) found nitrate concentrations to dilute in ~50% of rivers studied and the other half of the rivers were divided between no change with flow and increases with flow. SRP concentrations were found to dilute with higher flow in only 20% of the rivers, 40% of the rivers had no change and 40% increased. DOM and POM unanimously increased in all rivers (with the exception of no change in POM in the Gambia River). Many studies which focus on storm events are in watersheds with relatively steep slopes, seasonal precipitation patterns (Bhat et al. 2007; Rusjan et al. 2008), and rivers constantly fed by groundwater discharge (Hill 1993). There has been less research on storm events in flashy coastal systems, such as the Mission and Aransas rivers. This study emphasizes the importance of understanding system specific discharge-concentration relationships and incorporating timing of watershed exports into management practices.

Table 1: Land use and land cover (LULC) characteristics of the Mission and Aransas watersheds. LULC data was exported from a Geographic Information Systems (GIS) LULC layer provided by the National Oceanic and Atmospheric Administration (Figure 2).

LULC Category	Aransas River Watershed %	Mission River Watershed %
Developed	3.20	1.24
Cultivated	44.65	6.30
Pasture/Grassland	22.63	36.45
Forest	3.35	8.55
Scrub/Shrub	22.09	42.60
Wetlands	3.26	3.68
Shore/Bare land	0.24	0.37
Water	0.58	0.80

Table 2: Freshwater residence times in the tidal reaches of the Mission and Aransas rivers during low (5th percentile), annual median, and high (95th percentile) flow conditions. Physical data on the width, depth, and flow patterns within the tidal regions of the rivers were collected using a YSI Multiparameter Sonde and River Surveyor during summer 2008. Calculations of residence times were conducted by Stephanie Johnson, The University of Texas at Austin, Center for Research in Water Resources.

Site	Freshwater Residence times		
	Low Flow	Annual Median	High Flow
Aransas River	9-11 months	50 days	5 days
Mission River	5-6 months	22 days	<1 day

Table 3: Mission River export comparisons between 2007 and 2008. In the Mission River there were 12 events in 2007 and 1 event in 2008. Export reported in kg per year. A positive percent difference between LoadRunner and the manual load calculation of annual export indicates LoadRunner export was greater and a negative indicates the manual load calculation was greater.

	Annual export, LoadRunner		Annual export, mean conc x annual river discharge (manual load calc)		% of annual export during storms		% difference between LoadRunner and manual load calc	
	2007	2008	2007	2008	2007	2008	2007	2008
Nitrate	27310	363	22097	249	94	11	19	31
Ammonium	10247	140	8624	150	93	8	16	-7
SRP	12666	160	10806	209	93	8	15	-23
DOC	2862875	28057	2255288	31437	96	6	21	-11
DON	150957	1566	128181	1630	96	6	15	-4
POC	474313	6679	374572	8549	93	7	21	-22
PON	79484	1030	60996	1299	95	6	23	-21

Table 4: Aransas River export comparisons between 2007 and 2008. In the Aransas River there were 10 events in 2007 and 2 events in 2008. Export is reported in kg per year. A positive percent difference between LoadRunner and the manual load calculation of annual export indicates LoadRunner export was greater and a negative indicates the manual load calculation was greater.

	Annual export, LoadRunner		Annual export, mean conc x annual river discharge (manual load calc)		% of annual export during storms		% difference between LoadRunner and manual load calc	
	2007	2008	2007	2008	2007	2008	2007	2008
Nitrate	49108	19556	75580	29603	53	15	-35	-34
Ammonium	3454	540	3781	432	84	62	-9	20
SRP	24563	8983	32961	15050	59	15	-26	-40
DOC	615497	71232	589858	64256	90	59	4	10
DON	33344	3682	30432	2961	91	65	9	20
POC	300533	20460	157839	21133	96	76	48	-3
PON	43954	3114	234428	3169	95	75	47	-2

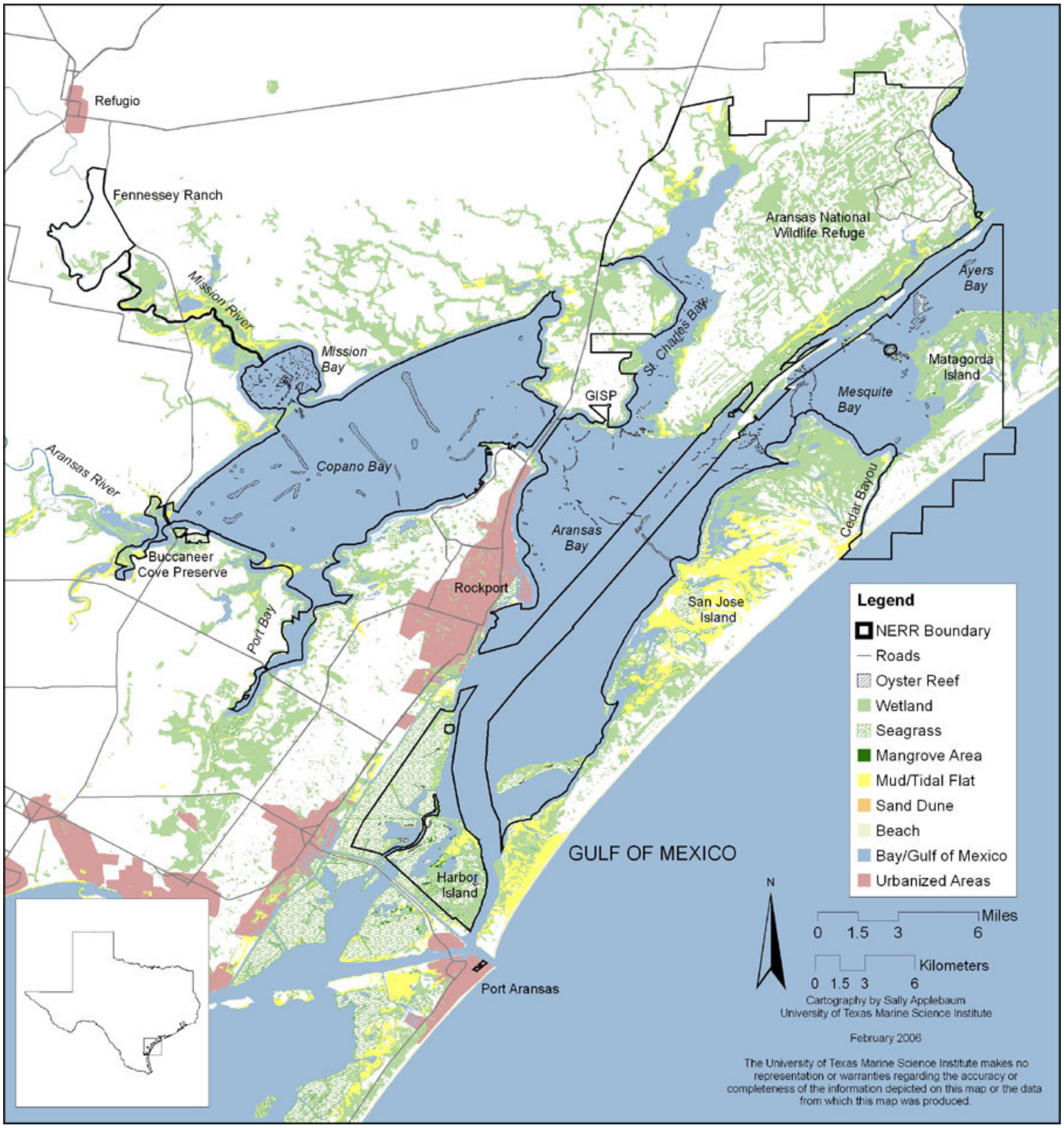


Figure 1: Map of the Mission-Aransas National Estuarine Research Reserve.

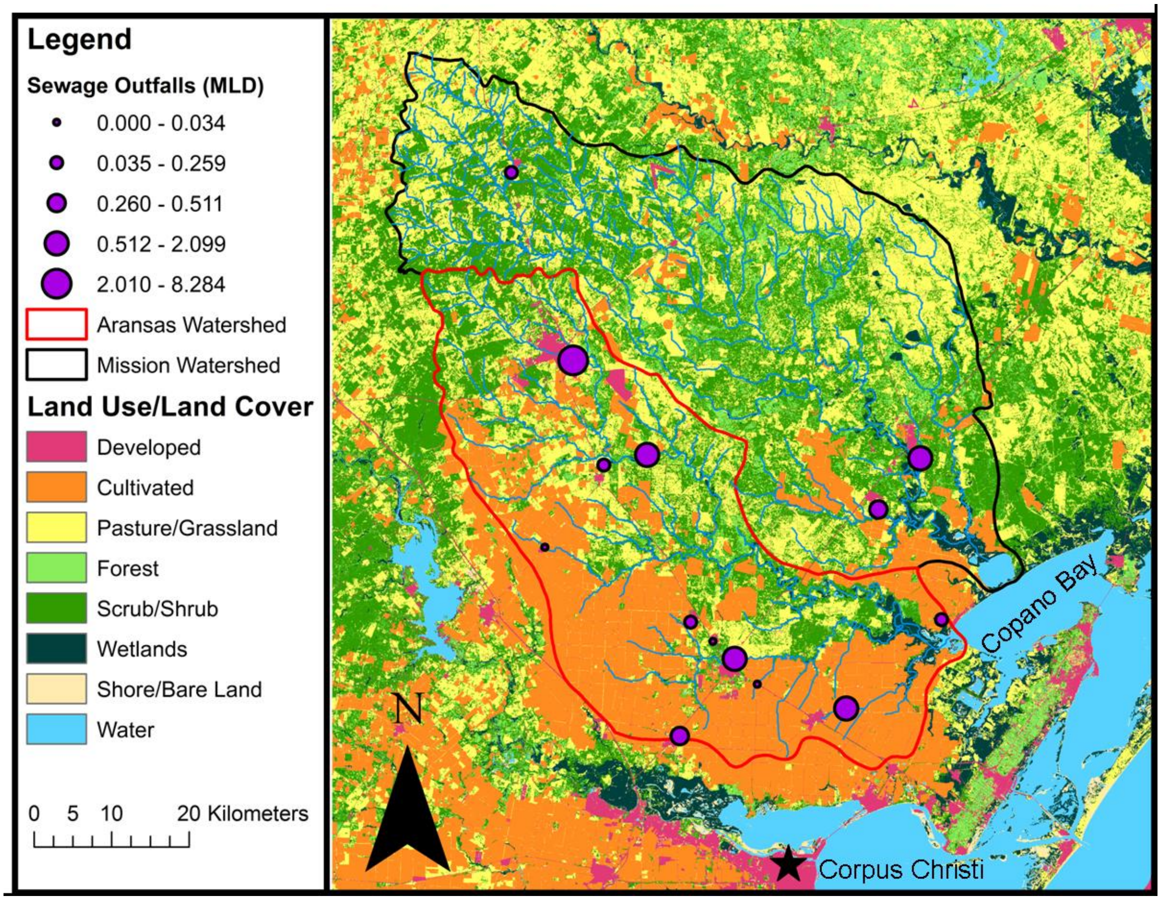


Figure 2: Mission and Aransas watersheds with land use and land cover (LULC). LULC (2005) downloaded from the National Oceanic and Atmospheric Administration Coastal Services Center's Coastal Change Analysis Program (C-CAP; http://www.csc.noaa.gov/crs/lca/ccap.html).

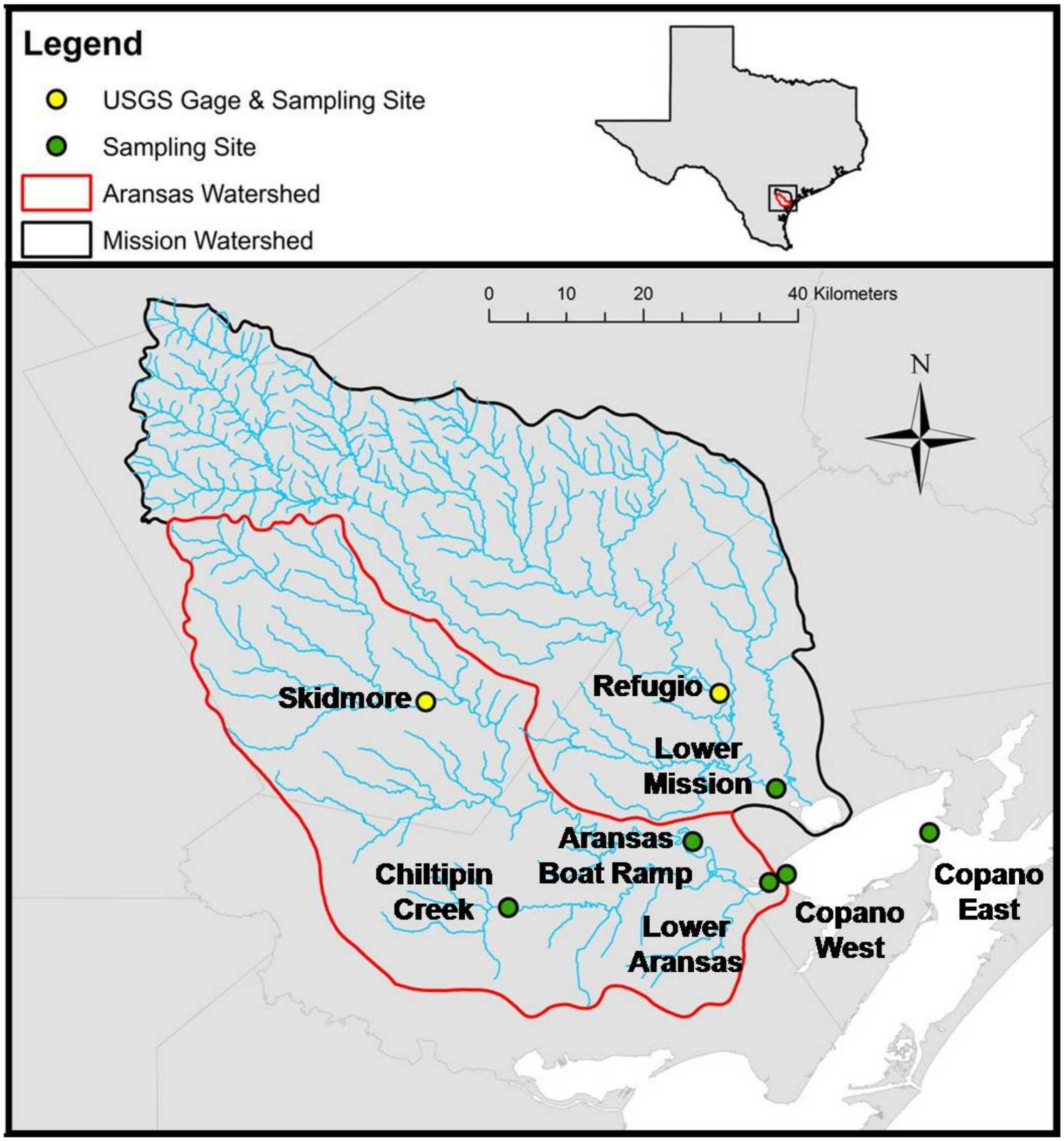


Figure 3: Mission and Aransas watersheds with riverine and estuarine sampling sites.

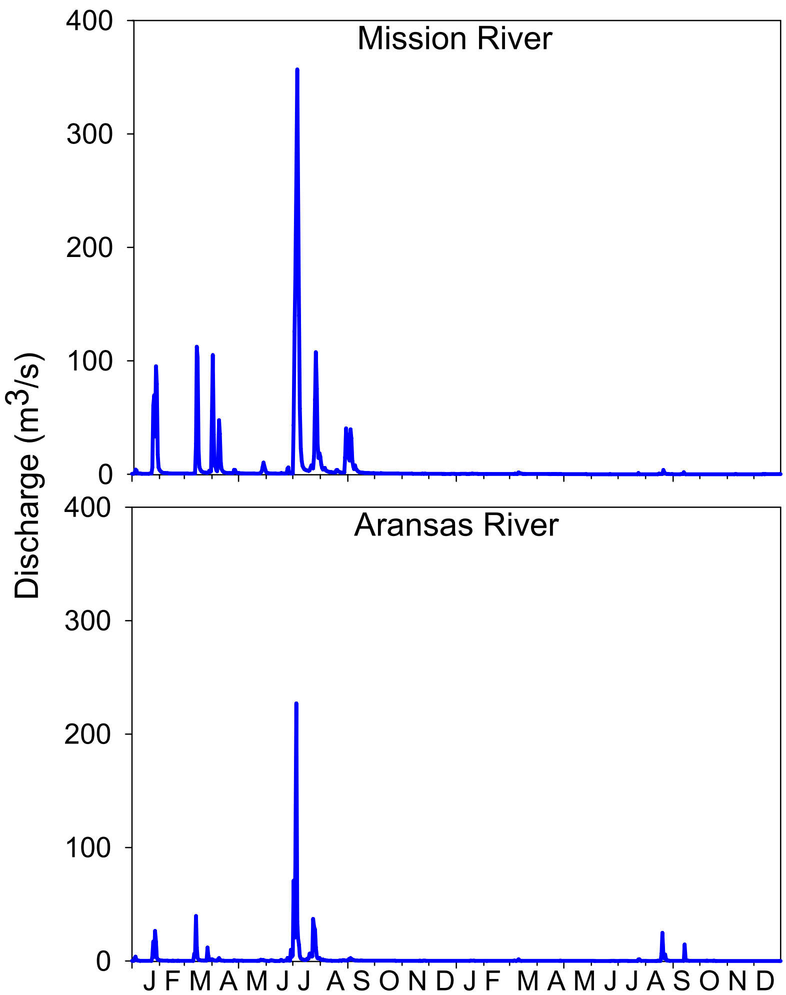


Figure 4: River discharge from the USGS gages, January 1, 2007 to December 31, 2008, in Refugio on the Mission River (top) and near Skidmore on the Aransas River (bottom).

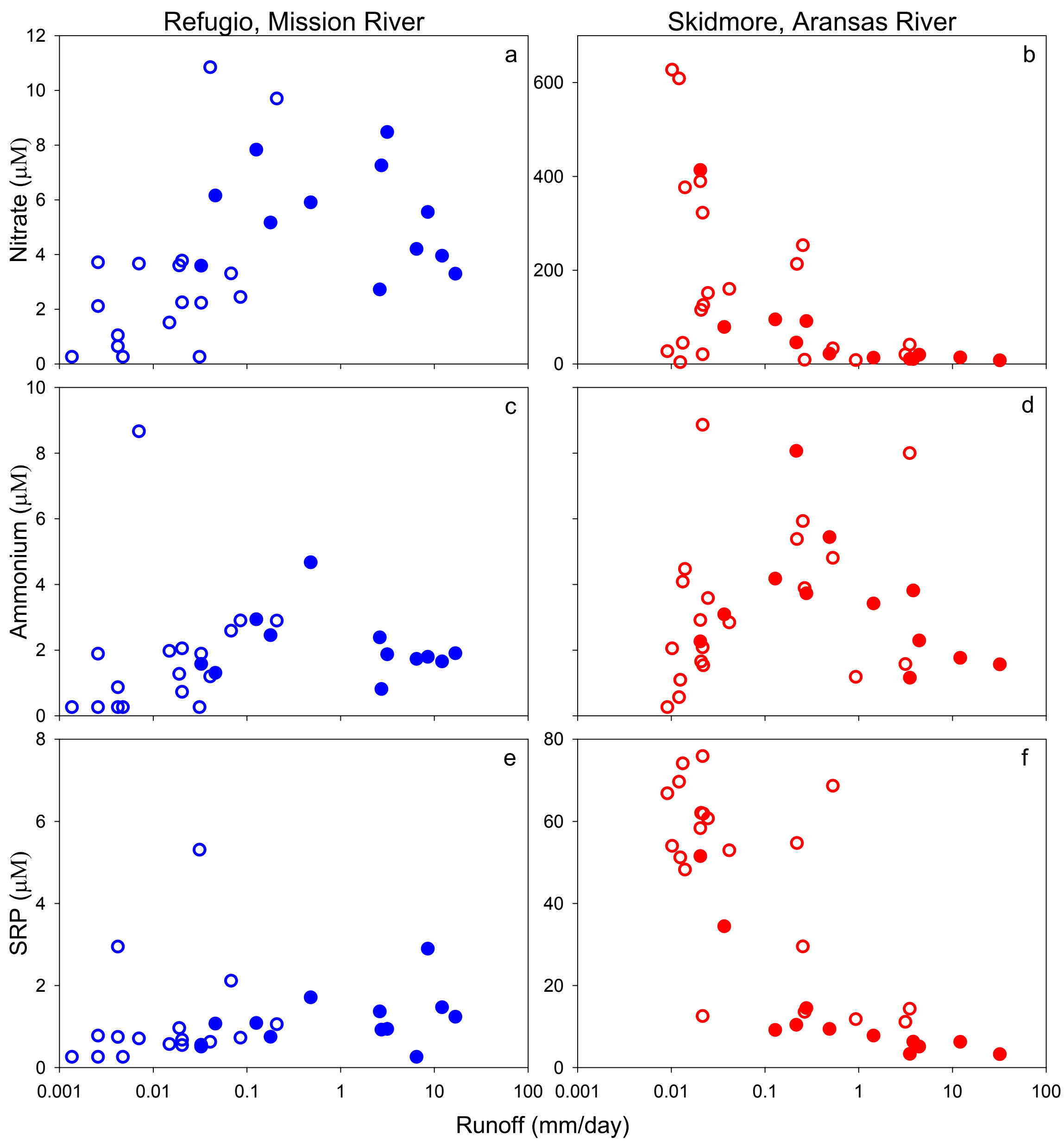


Figure 5: Nitrate, ammonium, and soluble reactive phosphorus (SRP) versus runoff at the upper Mission River site in Refugio and the upper Aransas River site near Skidmore. Data from 2007 are presented as closed circles (●) and data from 2008 are open circles (○). Runoff (mm/day) was used for all analyses to facilitate comparisons across watersheds.

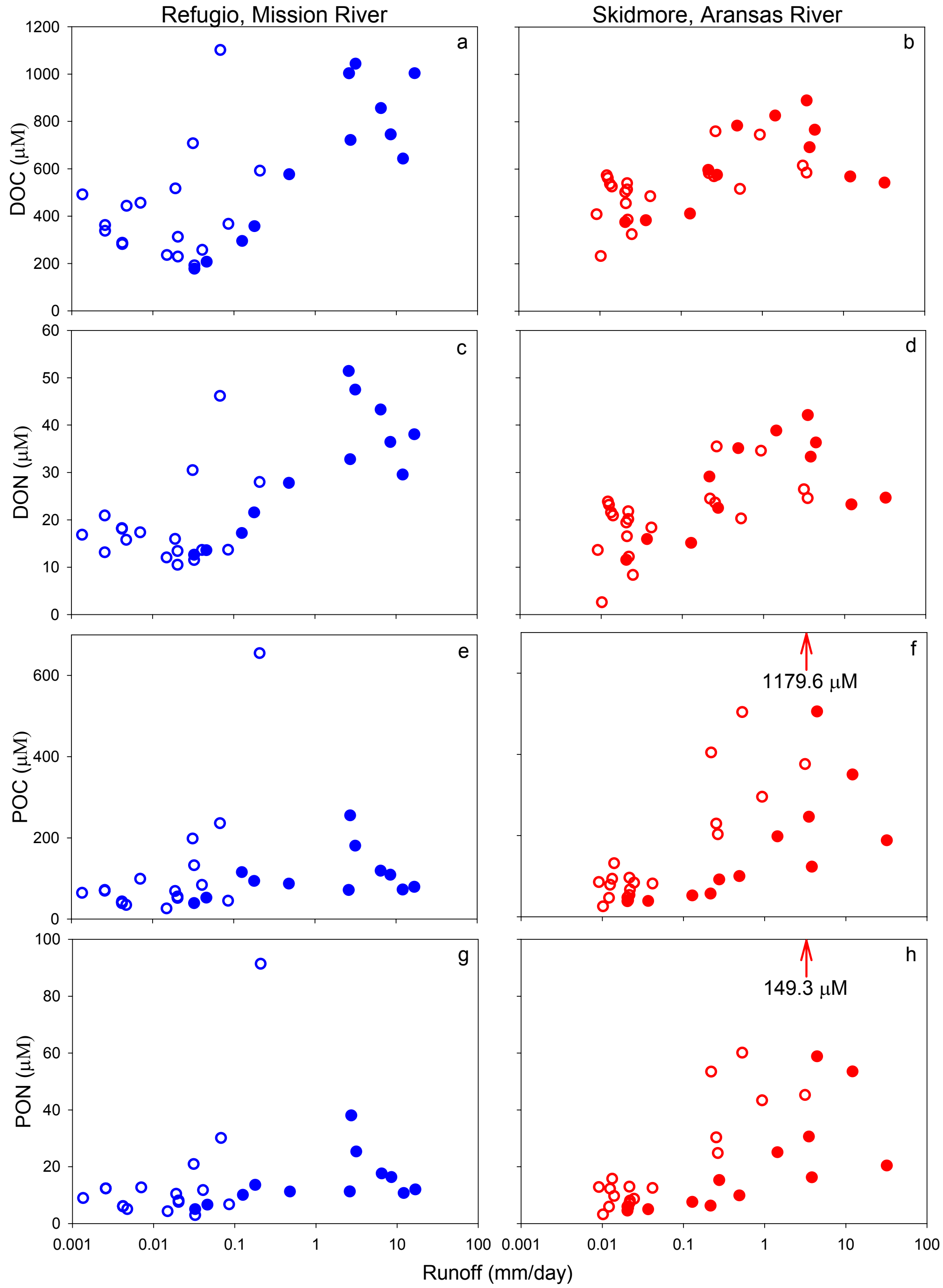


Figure 6: Dissolved organic carbon (DOC), dissolved organic nitrogen (DON), particulate organic carbon (POC), and particulate organic nitrogen (PON) versus runoff at upstream sites, Refugio, Mission River and Skidmore, Aransas River. Data from 2007 are presented as closed circles (●) and data from 2008 are open circles (○).

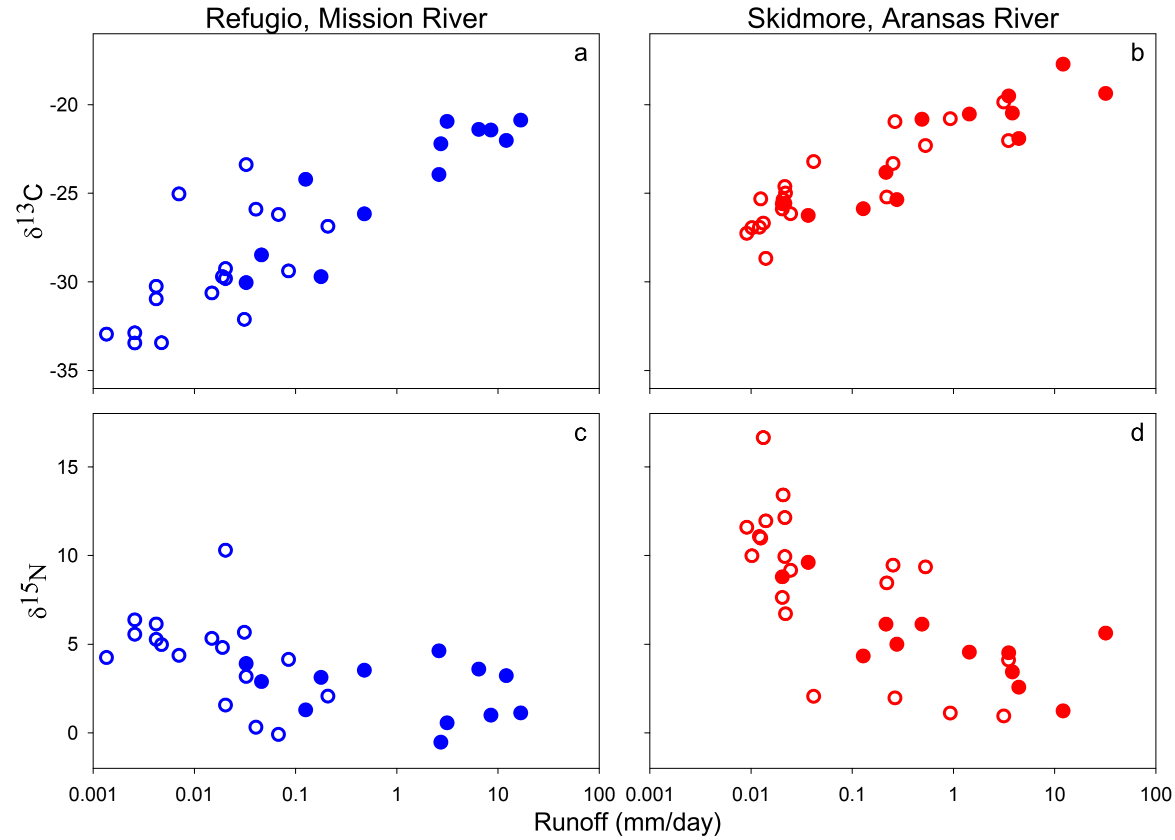


Figure 7: Stable carbon and nitrogen isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) of POM versus runoff at the upstream sites, Refugio on the Mission River and Skidmore on the Aransas River. Data from 2007 are presented as closed circles (●) and data from 2008 are open circles (○).

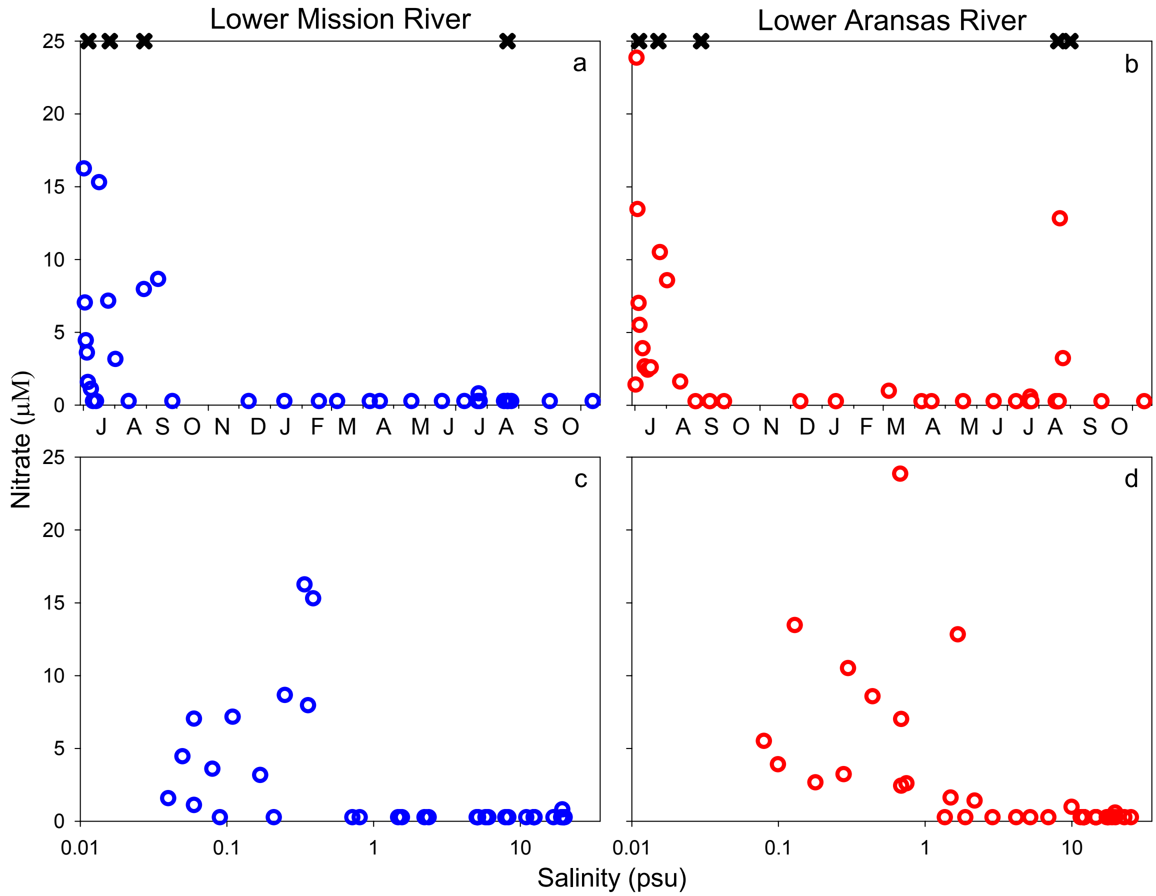


Figure 8: Nitrate concentrations versus time and salinity at the Lower Mission River and the Lower Aransas River sites. Storm events (determined by discharge changes as described in the Methods section) are indicated by an x on the top of panels a and b.

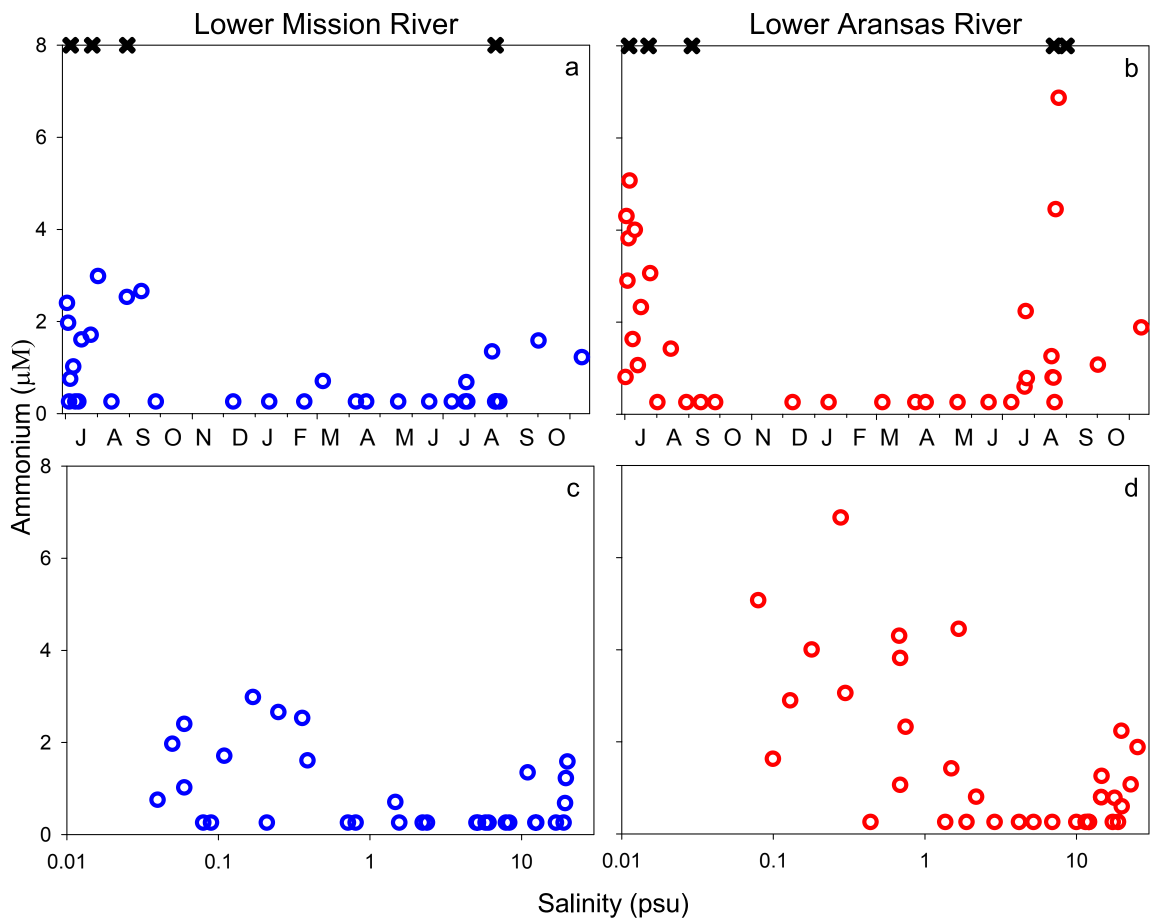


Figure 9: Ammonium concentrations versus time and salinity at the Lower Mission River and Lower Aransas River sites. Storm events are indicated by an x on the top of panels a and b.

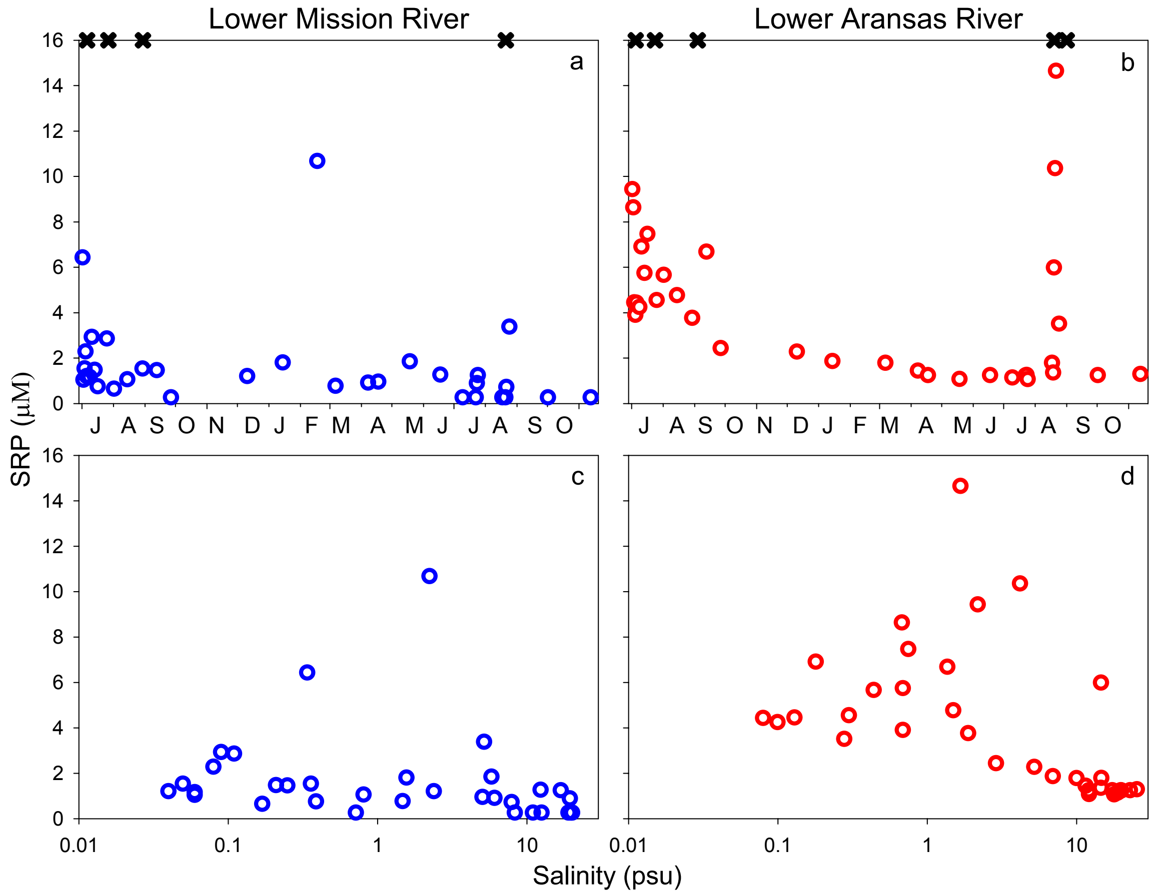


Figure 10: SRP concentrations versus time and salinity at the Lower Mission River and Lower Aransas River sites. Storm events are indicated by an x on the top of panels a and b.

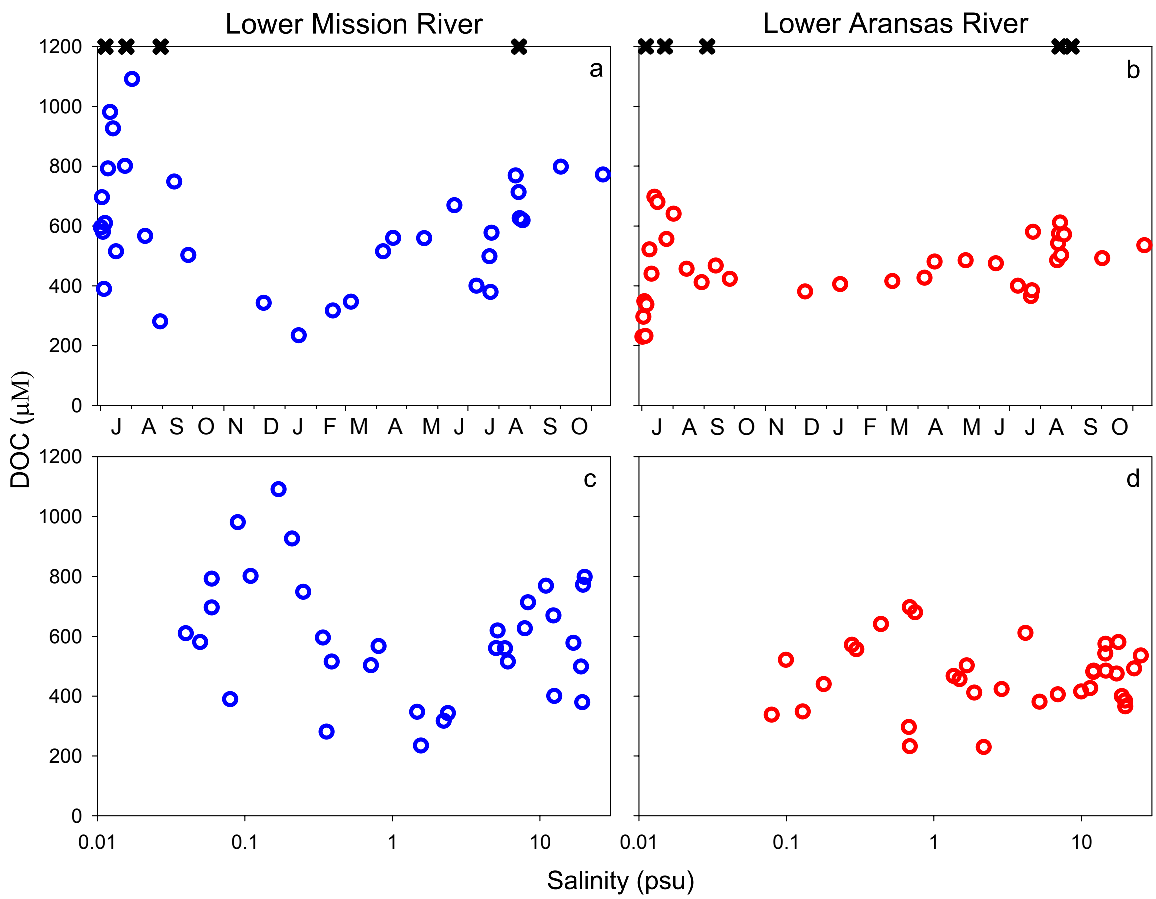


Figure 11: DOC concentrations versus time and salinity at the Lower Mission River and Lower Aransas River sites. Storm events are indicated by an X on the top of panels a and b.

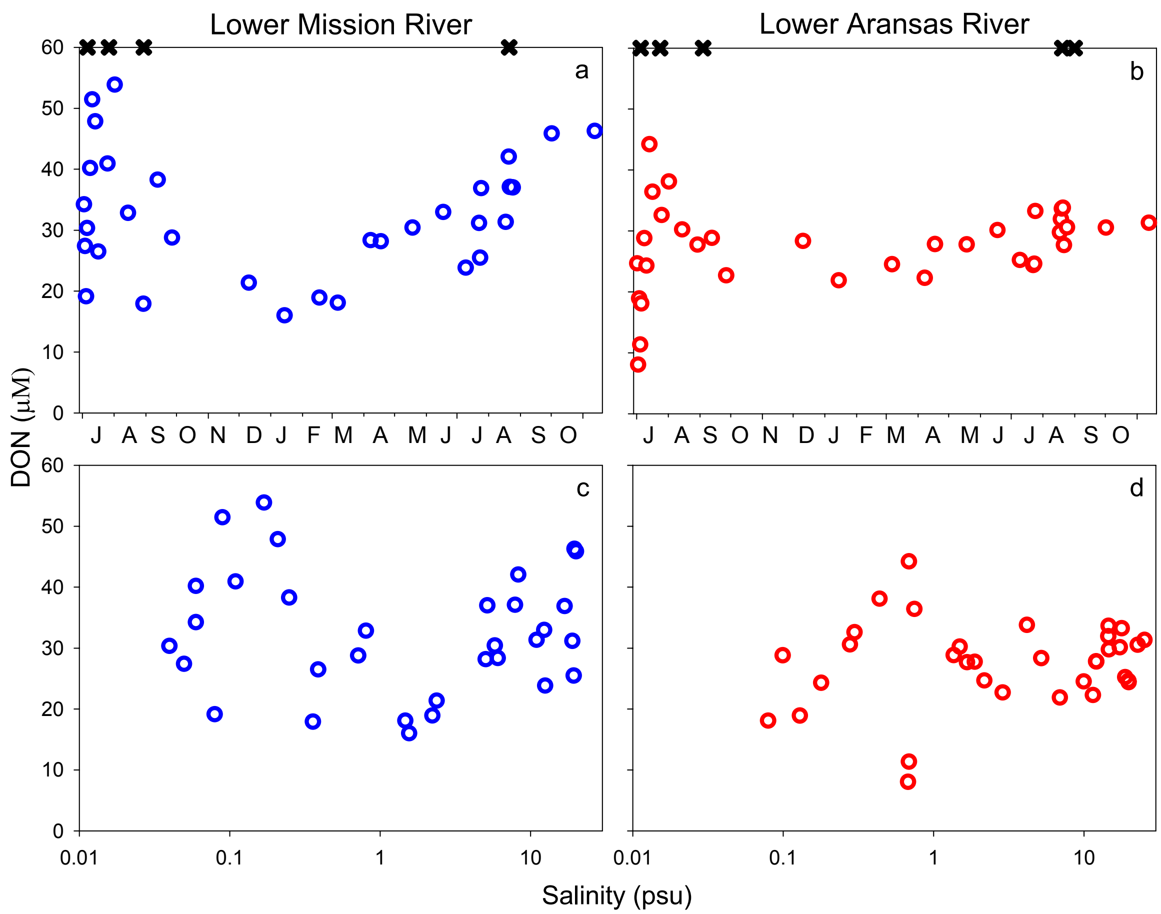


Figure 12: DON concentrations versus time and salinity at the Lower Mission River and Lower Aransas River sites. Storm events are indicated by an x on the top of panels a and b.

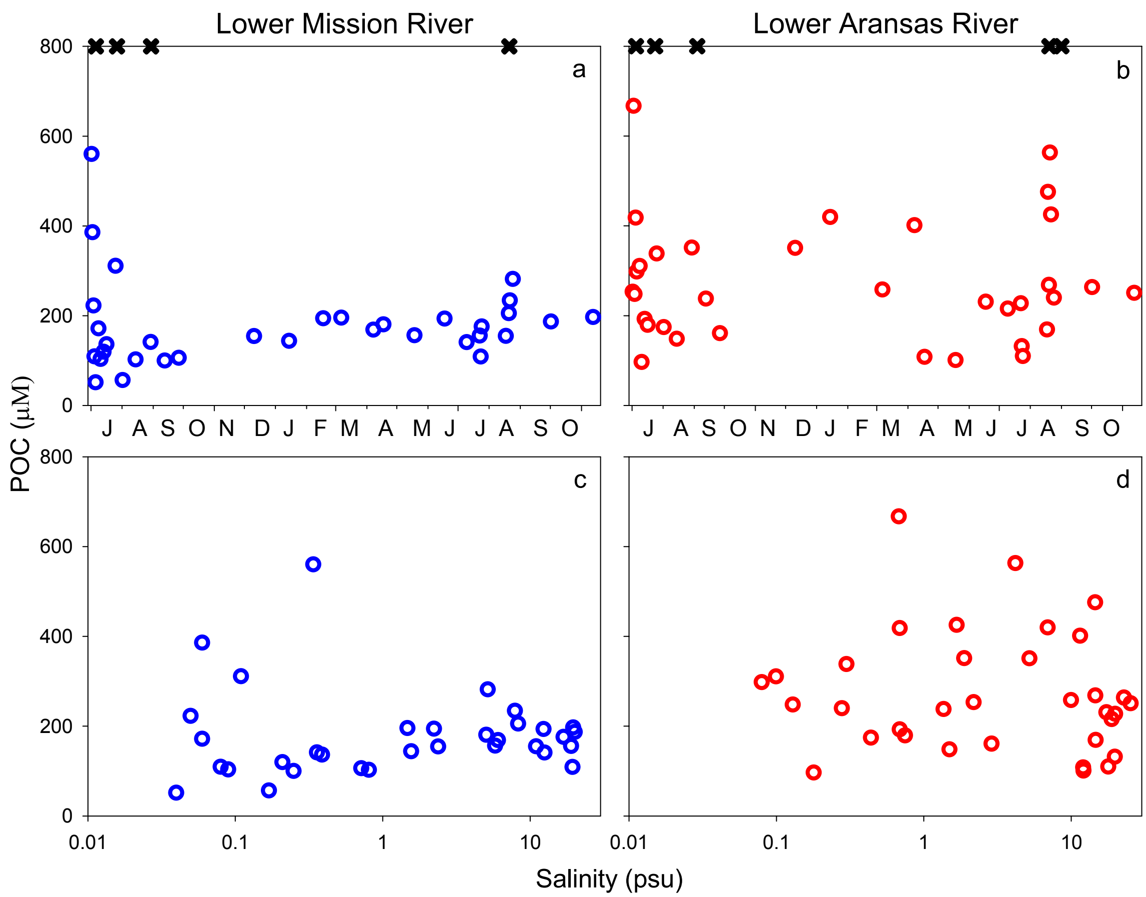


Figure 13: POC concentrations versus time and salinity at the Lower Mission River and Lower Aransas River sites. Storm events are indicated by an x on the top of panels a and b.

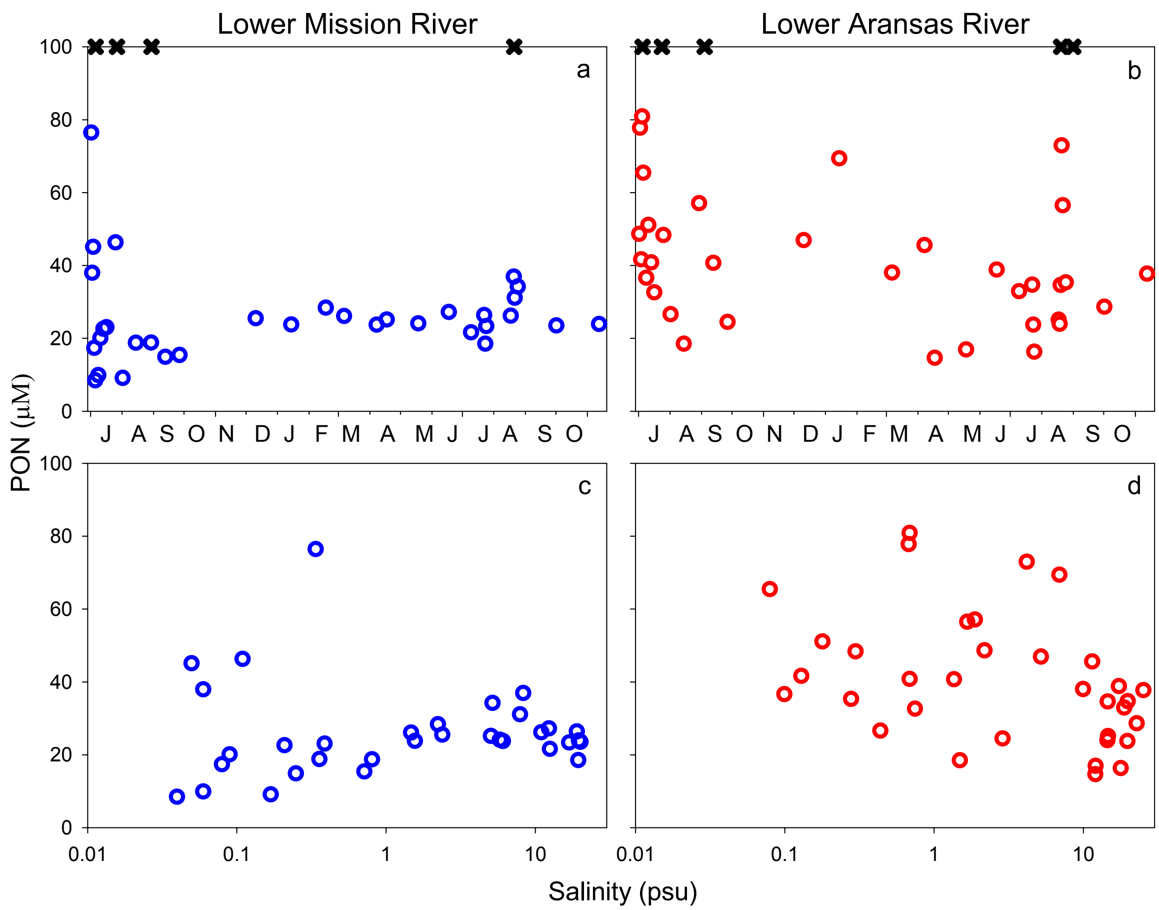


Figure 14: PON concentrations versus time and salinity at the Lower Mission River and Lower Aransas River sites. Storm events are indicated by an x on the top of panels a and b.

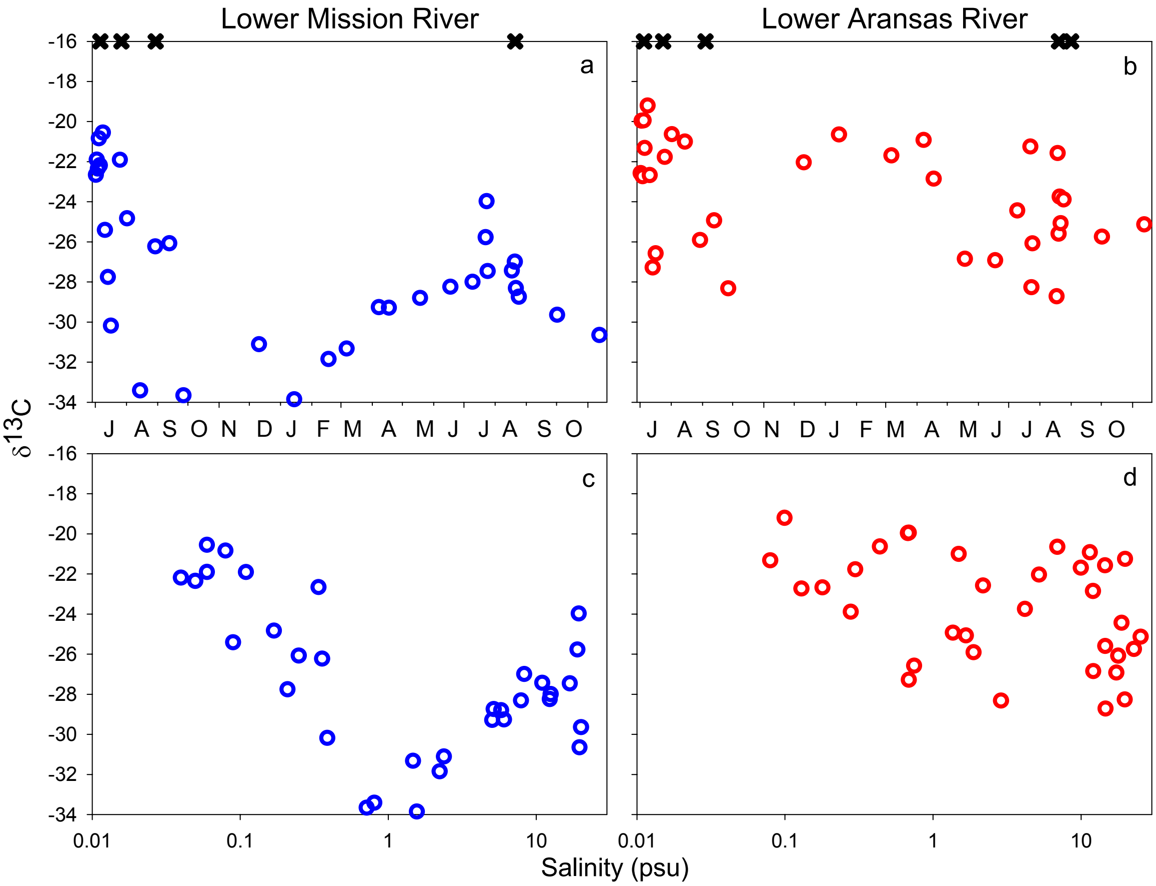


Figure 15: POC $\delta^{13}C$ versus time and salinity at the Lower Mission River and Lower Aransas River sites. Storm events are indicated by an x on the top of panels a and b.

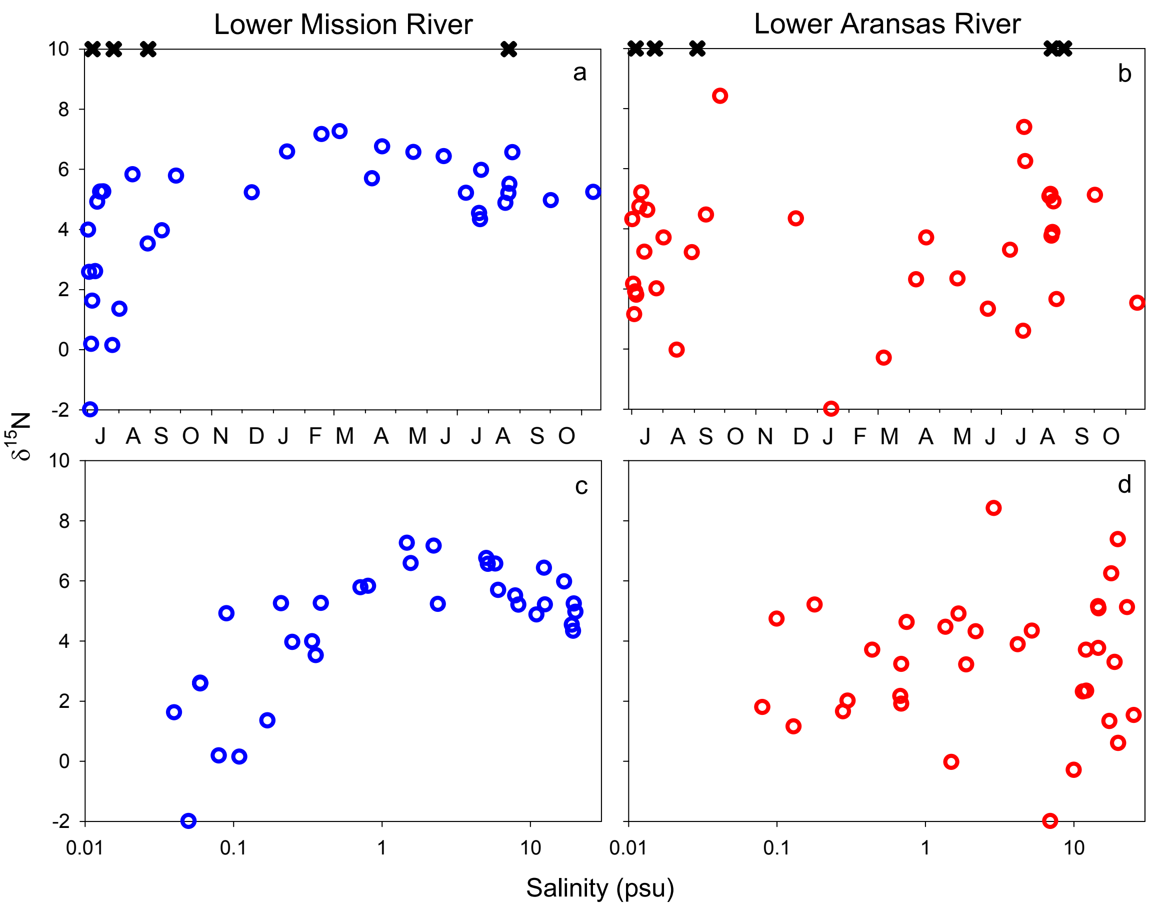


Figure 16: PON $\delta^{15}N$ versus time and salinity at the Lower Mission River and Lower Aransas River sites. Storm events are indicated by an X on the top of panels a and b.

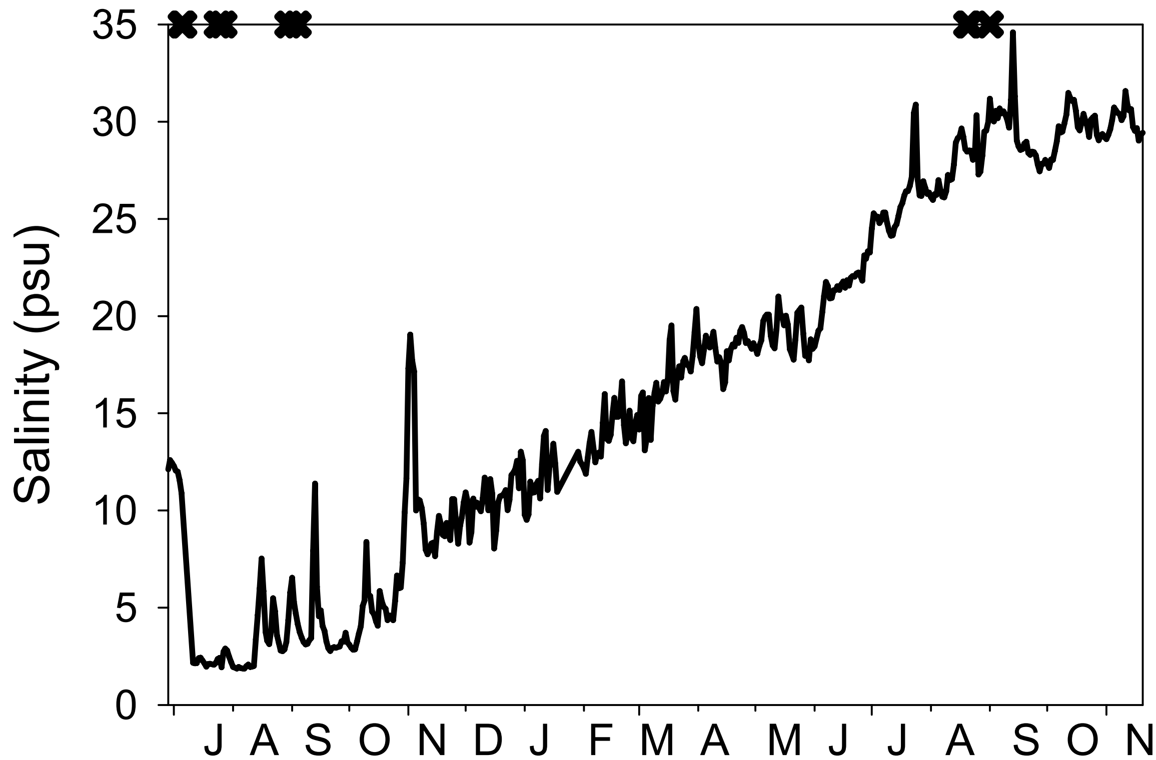


Figure 17: Salinity in Copano Bay at the Mission-Aransas NERR Copano East SWMP station from June 2007 to November 2008. Storm events (determined by discharge from upstream gages) are indicated by an x on the top of the figures.

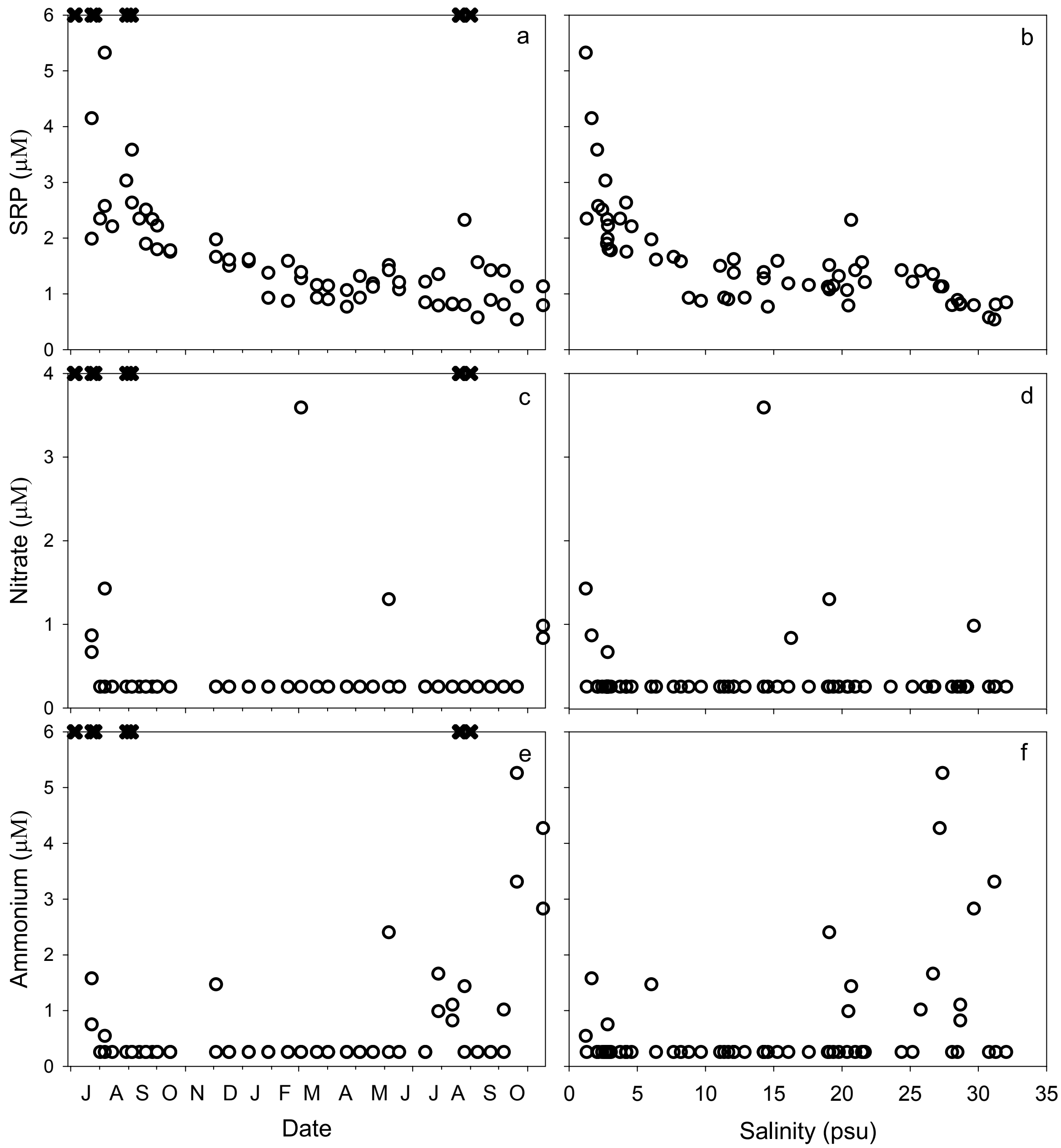


Figure 18: SRP, nitrate, and ammonium concentrations versus time and salinity in Copano Bay. Storm events are indicated by an X on the top of panels a, c, and e.

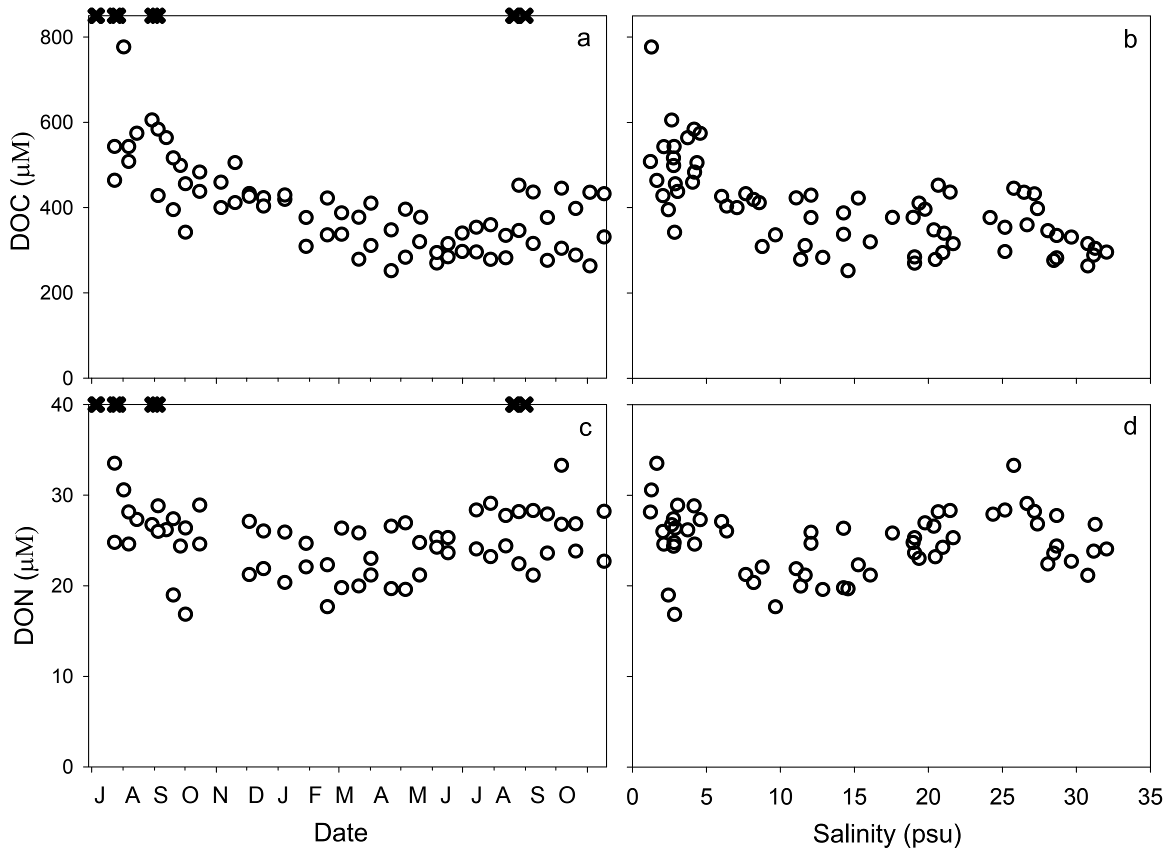


Figure 19: DOC and DON concentrations versus time and salinity in Copano Bay. Storm events are indicated by an X on the top of panels a and c.

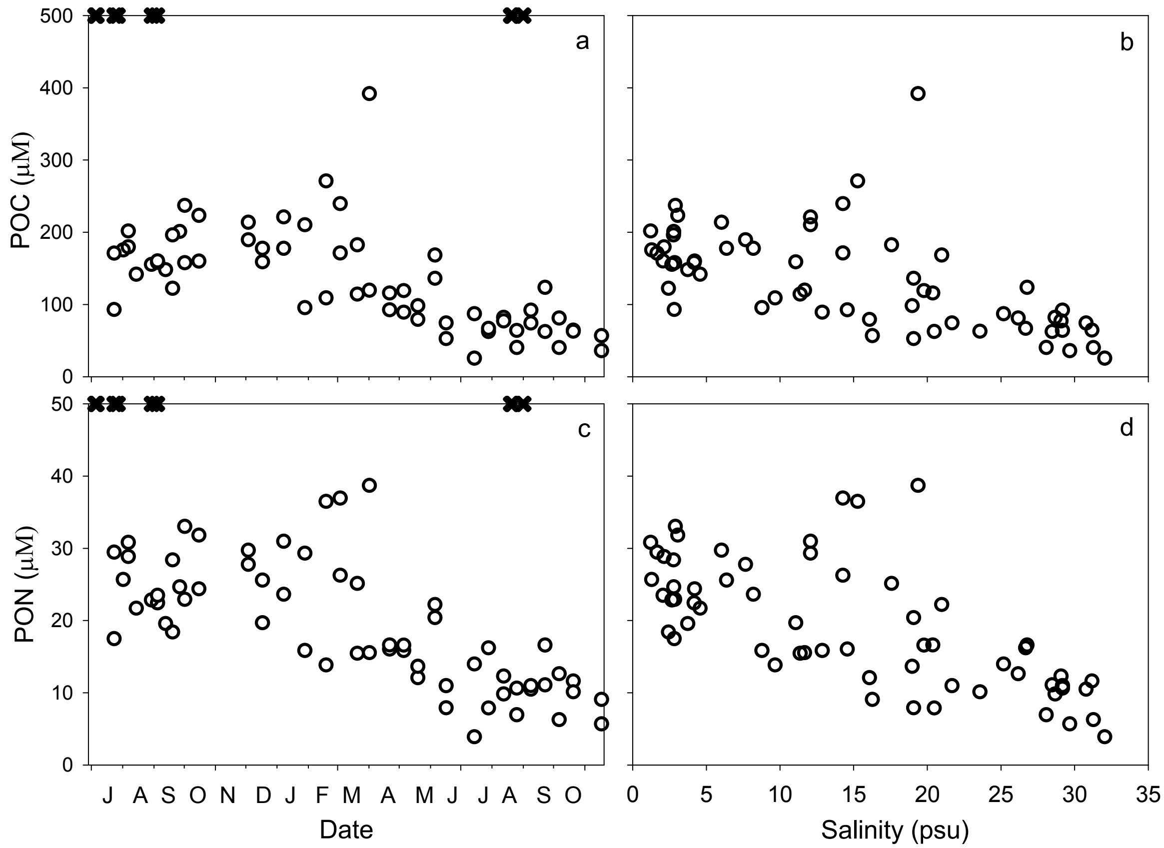


Figure 20: POC and PON concentrations versus time and salinity in Copano Bay. Storm events are indicated by an X on the top of panels a and c.

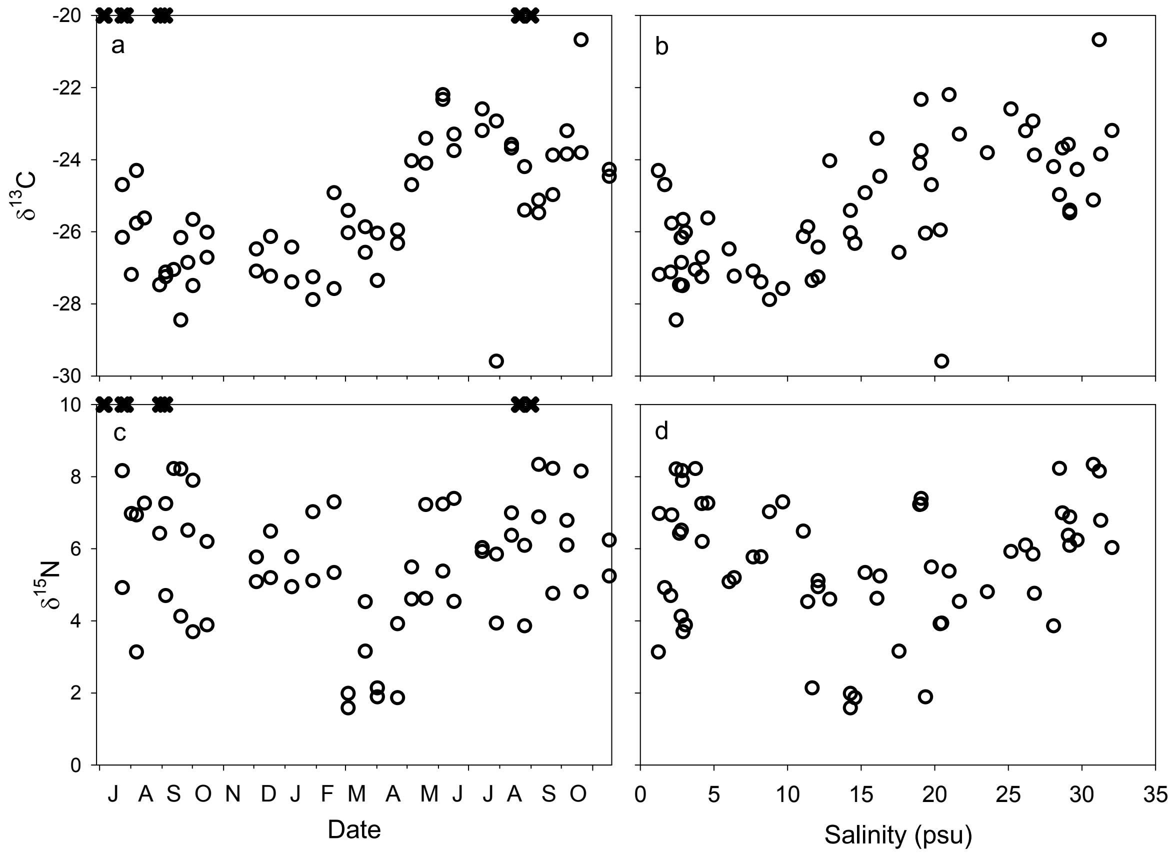


Figure 21: $\delta^{13}C$ and $\delta^{15}N$ of POM versus time and salinity in Copano Bay. Storm events are indicated by an x on the top of panels a and c.

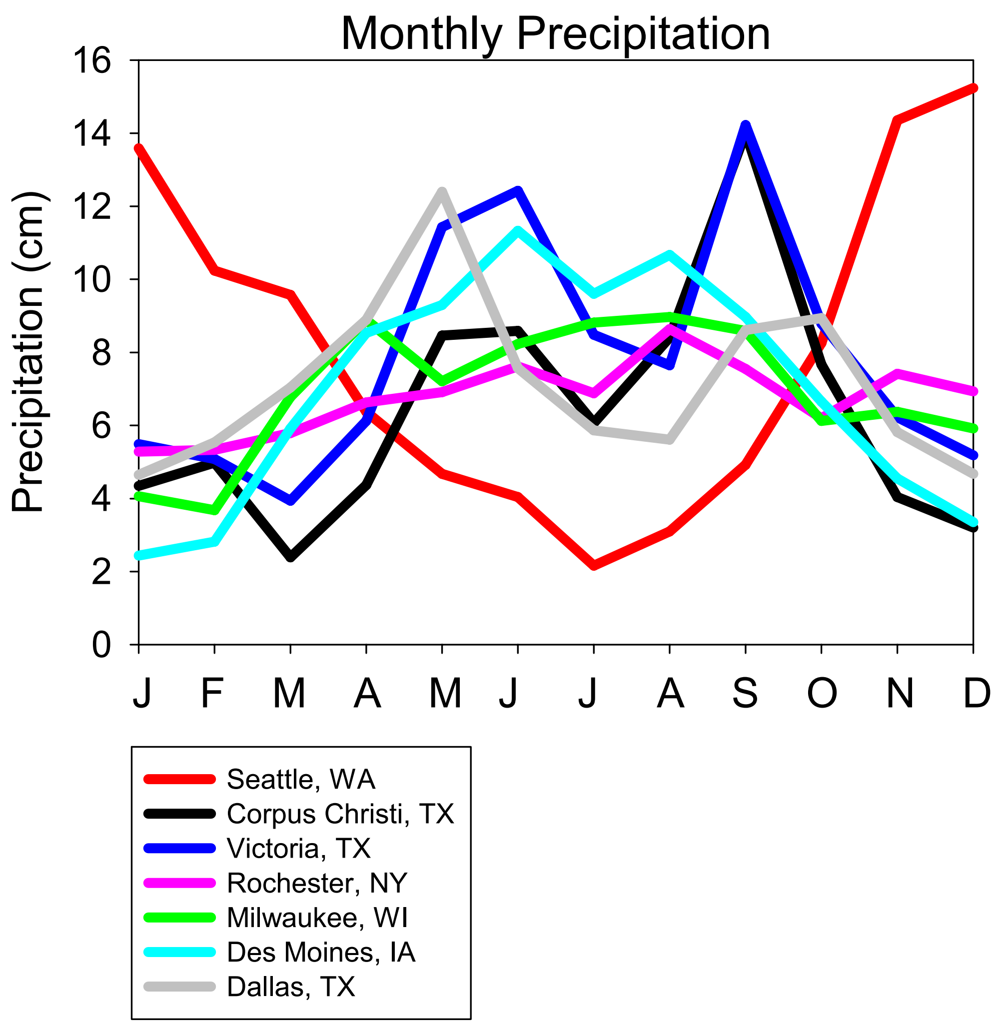


Figure 22: Monthly precipitation in select U.S. cities based on 30 years of data (The University of Utah 2009).

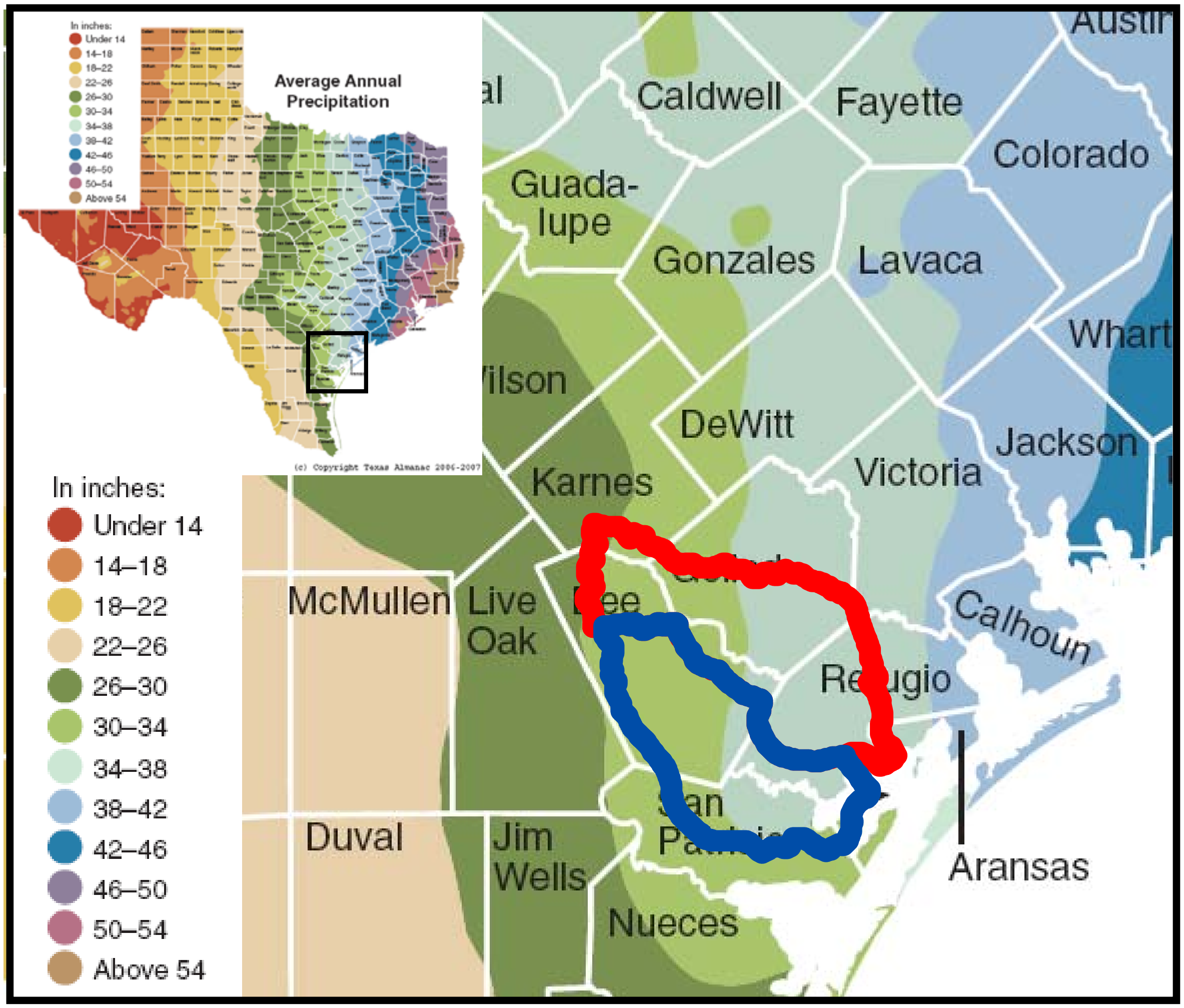


Figure 23: Precipitation patterns in Texas with counties displayed. The enlarged area includes the Mission (red) and Aransas (blue) Watersheds. Figure modified from the Texas Almanac (http://www.texasalmanac.com/).

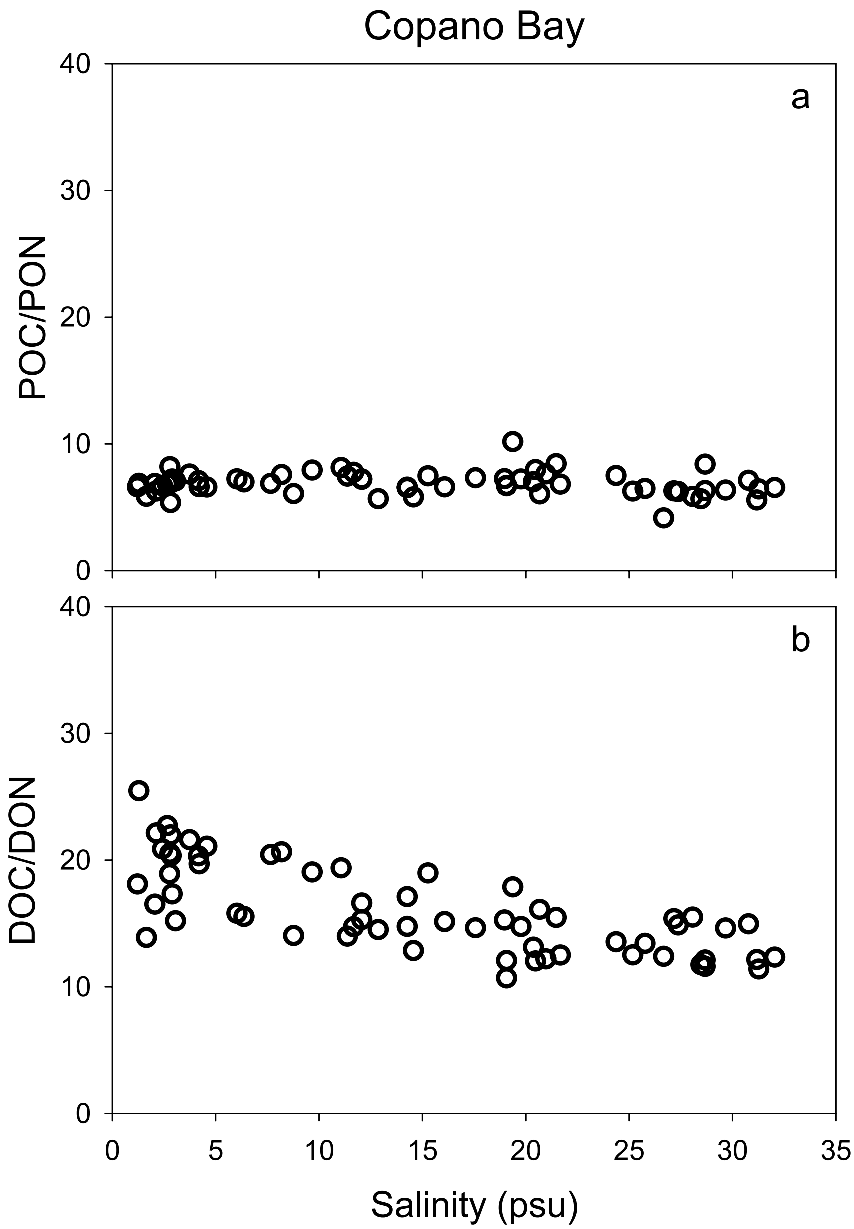


Figure 24: POC/PON (a) and DOC/DON (b) ratios versus salinity in Copano Bay.

Appendix A

LoadRunner statistical output from the Mission River at Refugio and the Aransas River near Skidmore, listed by river and constituent. Export reported in kg/d and concentrations in mg/L.

Mission River LoadRunner statistical results for concentration-discharge correlations. 29 samples were used to calibrate model.

Constituent	NO_3^-	NH_4^+	SRP	DOC	DON	POC	PON
Concentration r^2	45.92	35.09	18.57	47.34	55.35	25.04	20.48
a_0 coefficient	-2.6874	-3.4590	-3.3979	1.5643	-1.2363	0.2721	-1.7309
p-value (a_0)	1.4×10^{-12}	3.3×10^{-16}	8.0×10^{-17}	2.8×10^{-14}	5.8×10^{-14}	1.35×10^{-1}	2.6×10^{-10}
a_1 coefficient	0.2162	0.1388	0.0995	0.1218	0.1237	0.1070	0.1129
p-value (a_1)	2.6×10^{-4}	7.4×10^{-3}	3.5×10^{-2}	5.6×10^{-5}	2.2×10^{-6}	1.2×10^{-2}	1.2×10^{-2}
a_2 coefficient	-0.0584	-0.0536	-0.0244	0.0217	0.0118	-0.0267	-0.0098
p-value (a_2)	9.0×10^{-3}	9.6×10^{-3}	1.9×10^{-1}	4.5×10^{-2}	1.7×10^{-1}	1.1×10^{-1}	5.6×10^{-1}
Concentration minimum	8.00×10^{-3}	6.00×10^{-3}	0.01	4.0	0.22	0.49	0.10
Concentration maximum	0.11	0.05	0.05	14.0	0.69	1.77	0.29

Mission River LoadRunner statistical results for export-discharge correlations. 29 samples were used to calibrate model.

Constituent	NO_3^-	NH_4^+	SRP	DOC	DON	POC	PON
Export r^2	94.93	95.03	95.31	98.46	98.97	96.27	95.98
a_0 coefficient	3.0136	2.2420	2.3031	7.2653	4.4647	5.9731	3.9701
p-value (a_0)	$8.5x10^{-14}$	$1.8x10^{-11}$	$1.7x10^{-12}$	$6.0x10^{-33}$	$2.0x10^{-29}$	$5.4x10^{-25}$	$1.8x10^{-19}$
a_1 coefficient	1.2620	1.1388	1.0995	1.1218	0.1237	1.1070	1.1129
p-value (a_1)	$1.7x10^{-20}$	$1.3x10^{-20}$	$4.7x10^{-21}$	$4.0x10^{-28}$	$9.9x10^{-31}$	$1.6x10^{-22}$	$4.7x10^{-22}$
a_2 coefficient	-0.0584	-0.0536	-0.0244	0.0217	0.0118	-0.0267	-0.0098
p-value (a_2)	$9.0x10^{-3}$	$9.6x10^{-3}$	$1.9x10^{-1}$	$4.5x10^{-2}$	$1.7x10^{-1}$	$1.1x10^{-1}$	$5.6x10^{-1}$
Export minimum	0.02	0.01	0.04	11	0.54	1	0.24
Export maximum	2090	723	1166	438929	21336	43445	8768

Aransas River LoadRunner statistical results for concentration-discharge correlations. 31 samples were used to calibrate model.

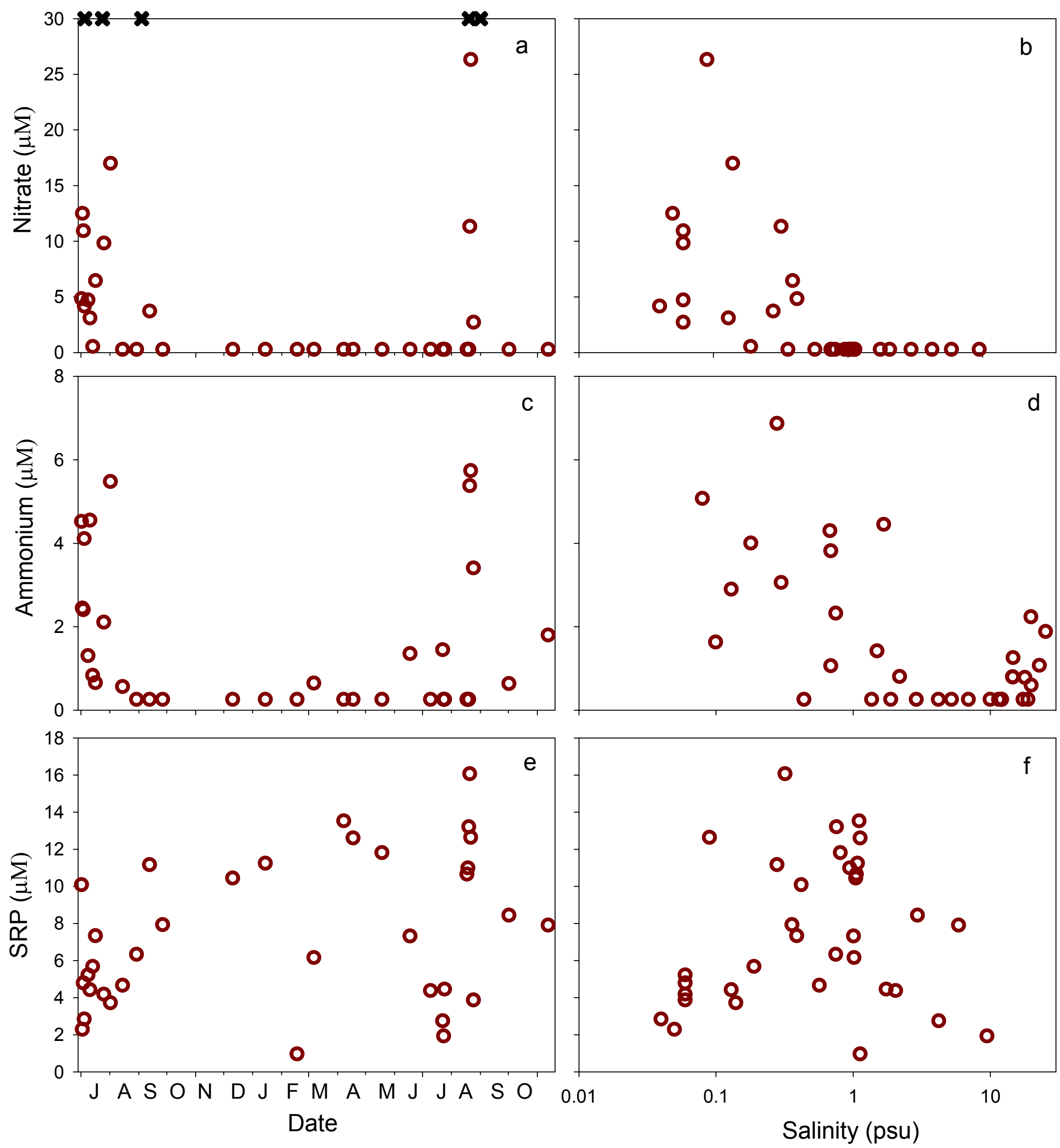
Constituent	NO_3^-	NH_4^+	SRP	DOC	DON	POC	PON
Concentration r^2	44.13	35.90	88.35	42.42	37.67	59.60	57.62
a_0 coefficient	-0.5238	-2.7808	-0.7708	2.0028	-0.9844	0.4558	-1.4339
p-value (a_0)	$1.3x10^{-1}$	$8.2x10^{-16}$	$1.9x10^{-8}$	$3.6x10^{-25}$	$6.0x10^{-9}$	$9.4x10^{-3}$	$1.4x10^{-9}$
a_1 coefficient	-0.4220	0.0788	-0.3950	0.0704	0.1236	0.2802	0.2773
p-value (a_1)	$2.2x10^{-5}$	$10.0x10^{-2}$	$4.0x10^{-16}$	$1.2x10^{-4}$	$3.9x10^{-4}$	$1.2x10^{-7}$	$2.6x10^{-7}$
a_2 coefficient	0.0042	-0.0890	0.0244	-0.0157	-0.0281	-0.0060	-0.0085
p-value (a_2)	$9.2x10^{-1}$	$5.6x10^{-4}$	$6.7x10^{-2}$	$5.8x10^{-2}$	$8.0x10^{-2}$	$7.7x10^{-1}$	$6.9x10^{-1}$
Concentration minimum	0.13	0.02	0.13	5.0	0.20	0.69	0.10
Concentration maximum	4.69	0.08	2.31	8.0	0.47	5.54	0.79

Aransas River LoadRunner statistical results for export-discharge correlations. 31 samples were used to calibrate model.

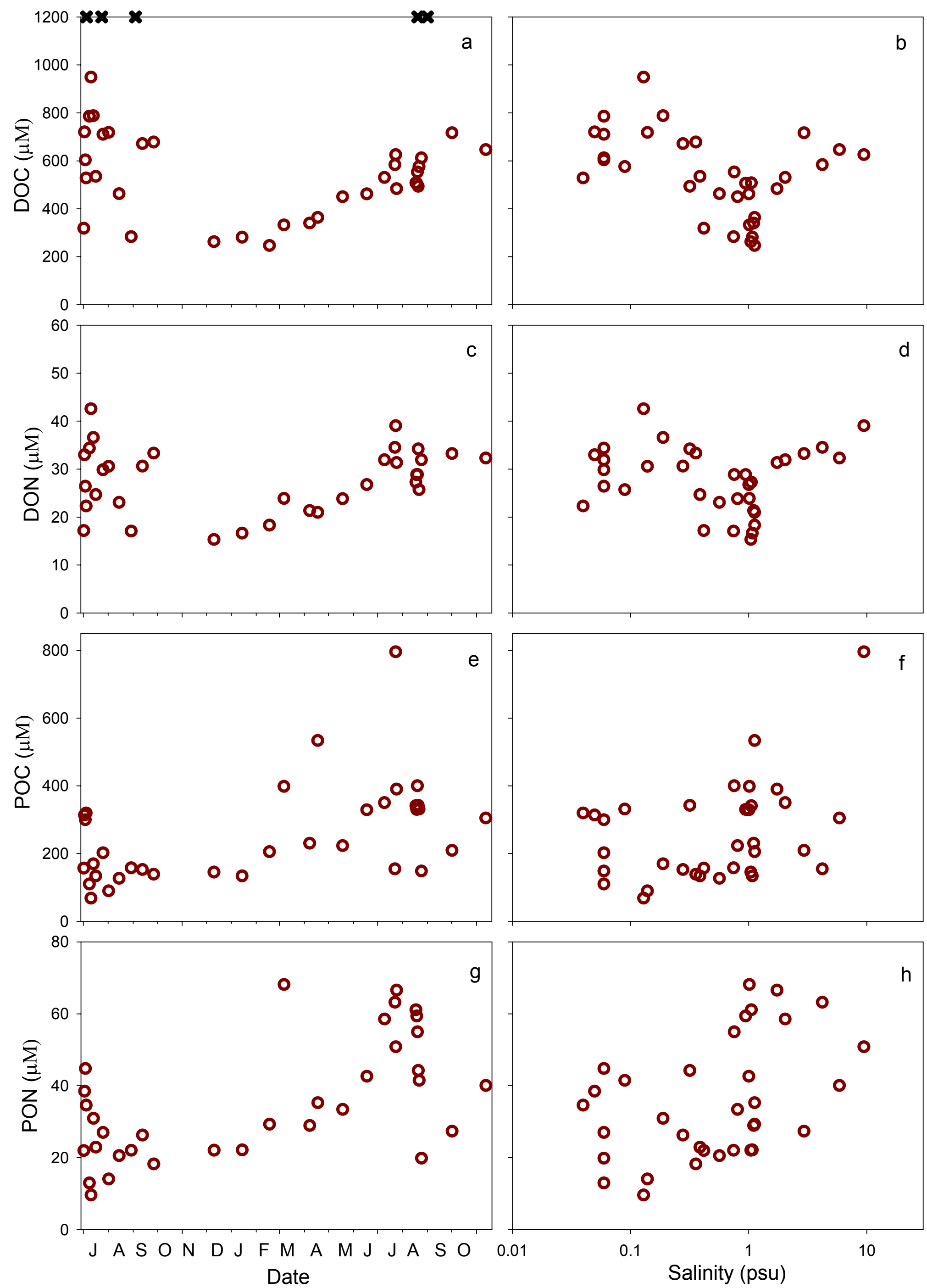
Constituent	NO_3^-	NH_4^+	SRP	DOC	DON	POC	PON
Export r^2	59.69	94.62	94.63	99.30	97.64	96.85	96.64
a_0 coefficient	4.7302	2.4732	4.4833	7.2569	4.269	5.7099	3.8201
p-value (a_0)	$5.4x10^{-15}$	$2.0x10^{-14}$	$1.5x10^{-29}$	$2.0x10^{-42}$	$2.2x10^{-26}$	$1.6x10^{-26}$	$7.0x10^{-21}$
a_1 coefficient	0.5780	1.0788	0.6050	1.0704	1.1236	1.2802	1.2773
p-value (a_1)	$1.11x10^{-7}$	$1.6x10^{-21}$	$1.9x10^{-21}$	$2.5x10^{-35}$	$4.5x10^{-27}$	$4.1x10^{-25}$	$1.1x10^{-24}$
a_2 coefficient	0.0042	-0.0890	0.0244	-0.0157	-0.0281	-0.0060	-0.0085
p-value (a_2)	$9.2x10^{-1}$	$5.6x10^{-4}$	$6.9x10^{-2}$	$5.8x10^{-2}$	$8.0x10^{-2}$	$7.72x10^{-1}$	$6.9x10^{-1}$
Export minimum	34	0.17	17	37	1	5	0.76
Export maximum	2596	290	2545	145778	7481	108725	15453

Appendix B

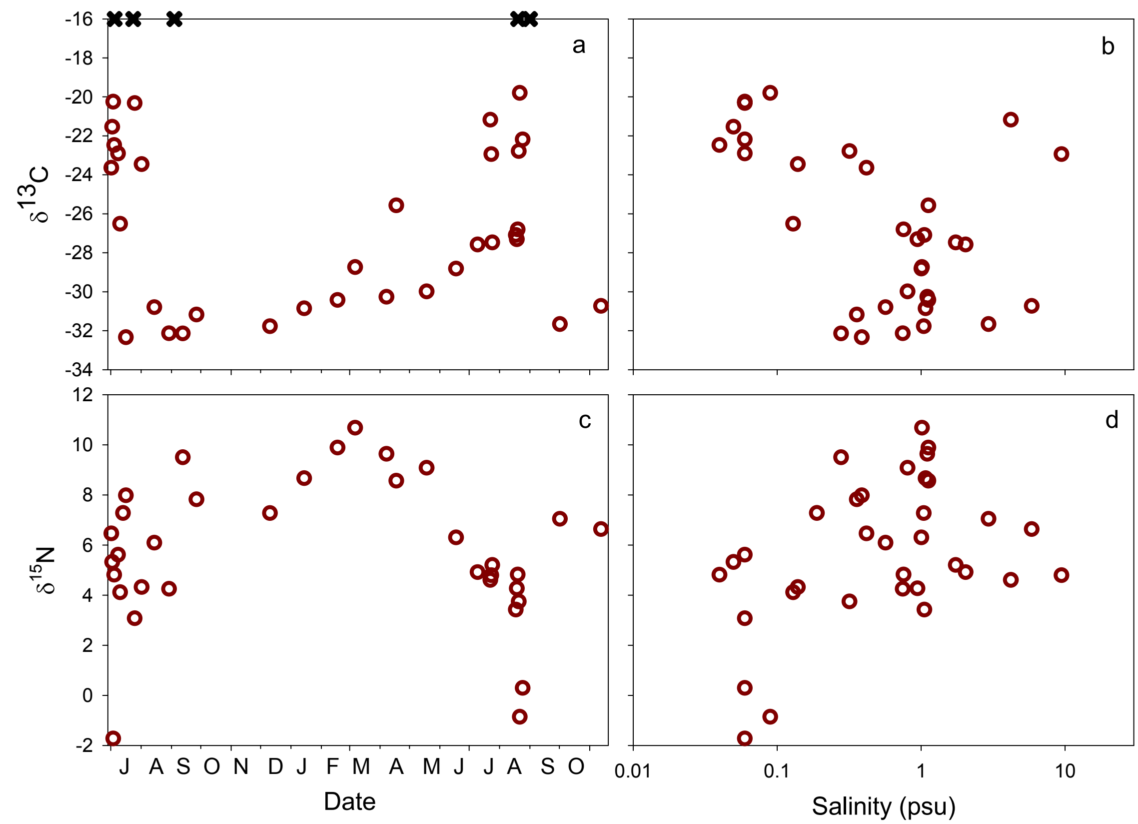
Results from the Aransas Boat Ramp site.



Concentrations of nitrate, ammonium, and SRP versus time (July 2, 2007 through November 13, 2008) and salinity. Storm events are indicated by an x on the top of panel a.



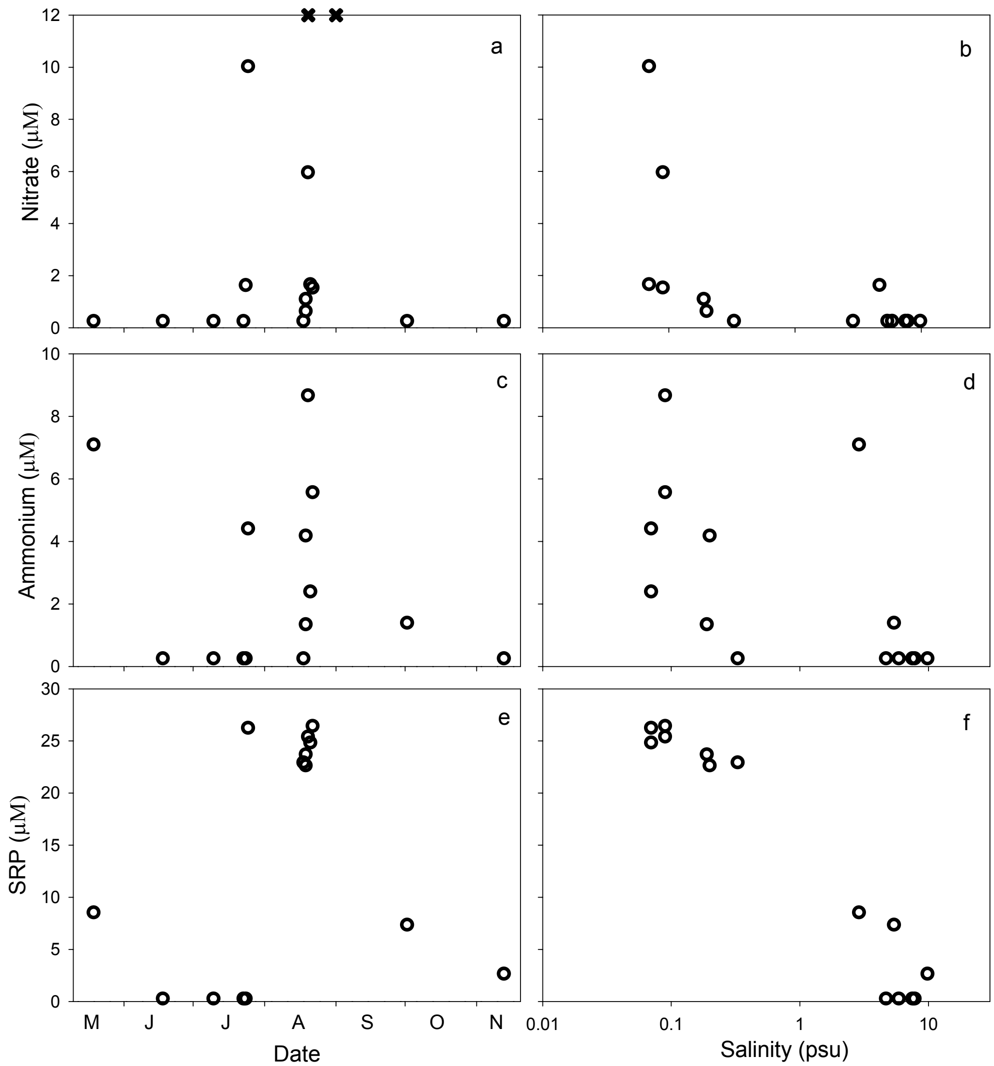
DOC, DON, POC, and PON concentrations versus time (July 2, 2007 through November 13, 2008) and salinity. Storm events are indicated by an x on the top of panel a.



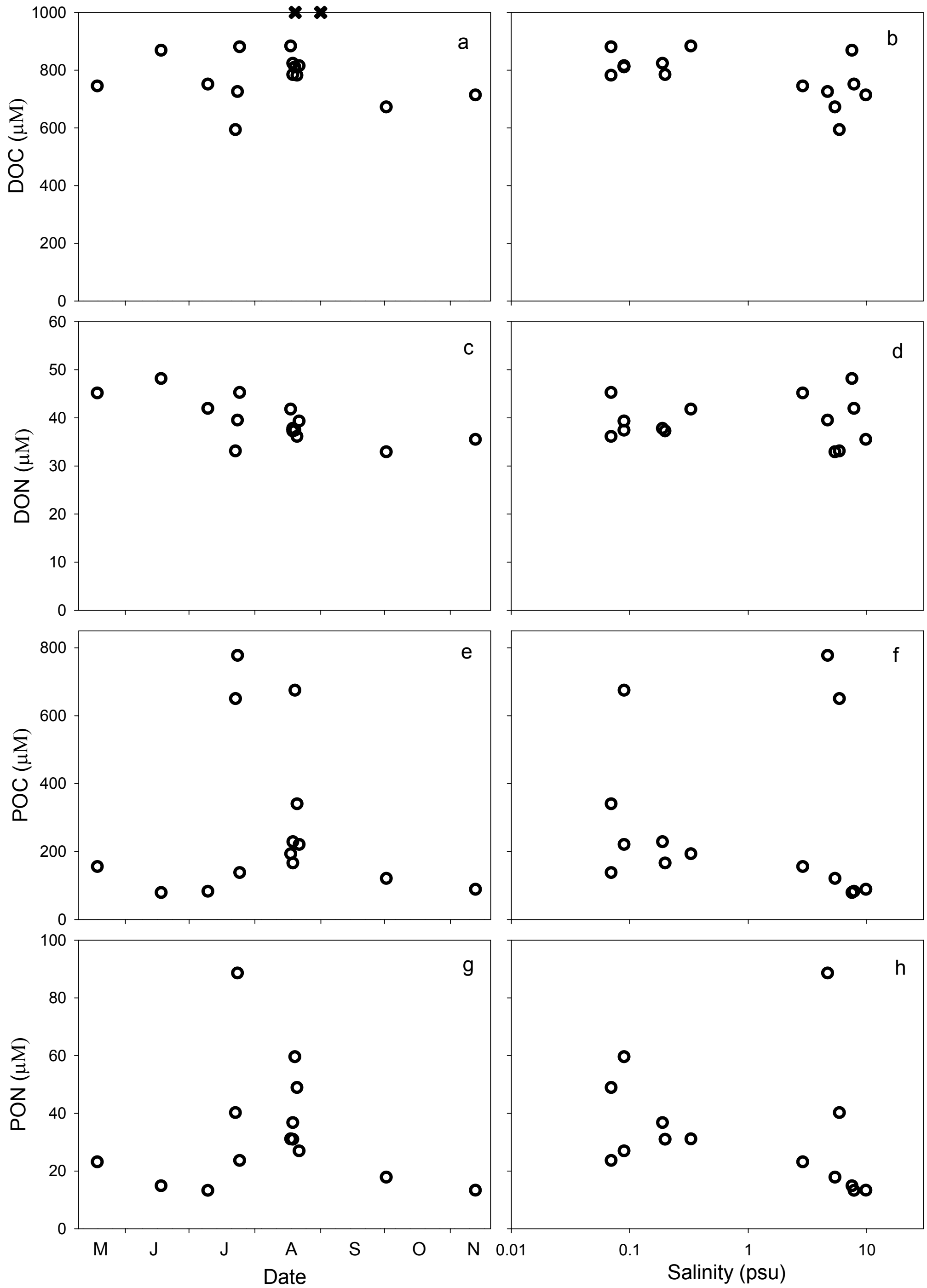
$\delta^{13}C$ and $\delta^{15}N$ of POM versus time (July 2, 2007 through November 13, 2008) and salinity. Storm events are indicated by an x on the top of panel a.

Appendix C

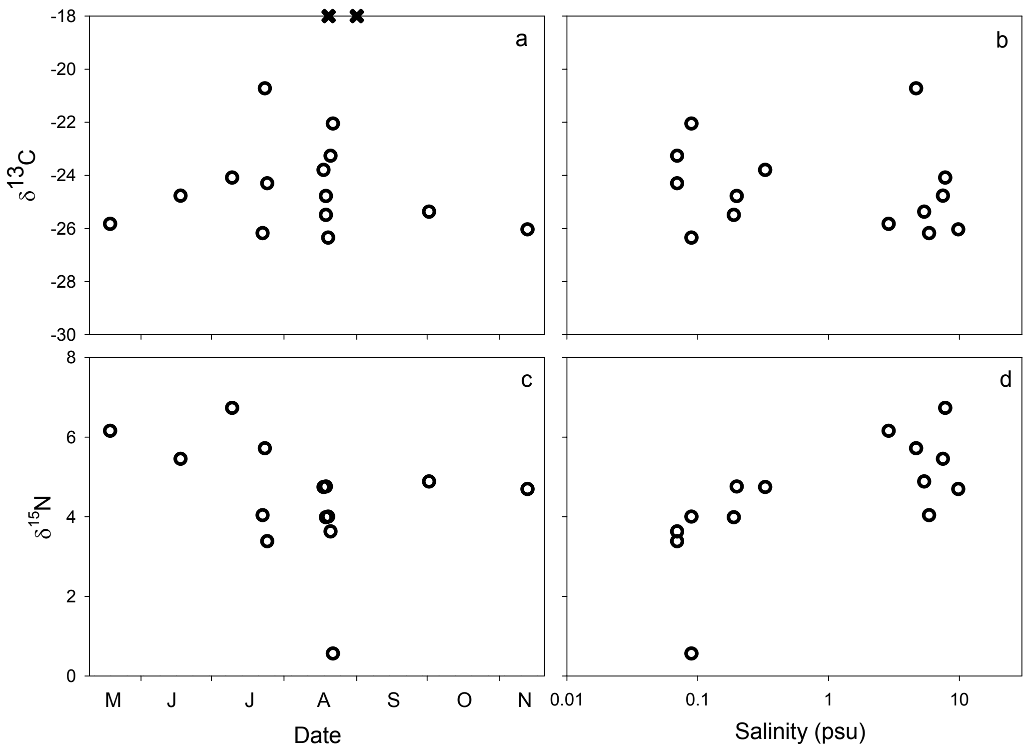
Results from the Chiltipin Creek site.



Nitrate, ammonium, SRP concentrations versus time (May 10, 2008 through November 13, 2008) and salinity. Storm events are indicated by an x on the top of panel a.



DOC, DON, POC, and PON concentrations versus time (May 10, 2008 through November 13, 2008) and salinity. Storm events are indicated by an x on the top of panel a.



$\delta^{13}C$ and $\delta^{15}N$ of POM versus time (May 10, 2008 through November 13, 2008) and salinity. Storm events are indicated by an x on the top of panel a.

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